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# AMERICAN CHEMICAL JOURNAL

EDITED BY

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# AMERICAN CHEMICAL JOURNAL

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Contributions from the Chemical Laboratory of Harvard College.

## CXIX.—ON NITROMALONIC ALDEHYDE.

[SECOND PAPER.]

BY HENRY B. HILL.

### ON THE CONDENSATION OF NITROMALONIC ALDEHYDE WITH CERTAIN KETONES AND KETONE-ACIDS.

BY CHARLES A. SOCH AND GEORGE OENSLAGER.

In a former paper<sup>1</sup> it was shown that nitromalonic aldehyde readily entered into reaction with acetone in alkaline solution, and that the product formed was *p*-nitrophenol. Certain results which had already been obtained by Messrs. Soch and Oenslager were also mentioned, which showed that the reaction could easily be extended to other ketones and to ketone-acids. Although their investigation was at that time essentially completed, a few experimental details still needed revision, and as both of these gentlemen had already left Cambridge, the publication of their results has necessarily been delayed.

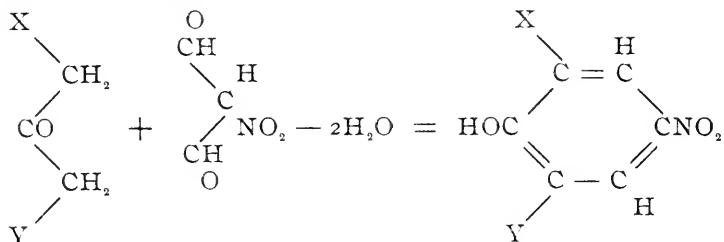
In order to establish the general nature of the reaction it seemed advisable to select for study a few typical ketones and ketone-acids, but to make no attempt to extend the investigation in such way as to cover a large number of bodies

<sup>1</sup> This JOURNAL, 22, 89.

which might easily be prepared. Methylethyl ketone and dibenzyl ketone were accordingly selected as typical ketones, while acetacetic ester, levulinic acid and acetone dicarboxylic acid were chosen to represent the ketone-acids. Certain other bodies of similar nature, which promise to yield condensation products of peculiar interest, may be studied in the future.

It was found that condensation took place most neatly in dilute (normal) aqueous solution with the addition of a slight excess of sodic hydrate. With acetacetic ester two molecules of sodic hydrate were needed, and saponification of the ester doubtless preceded the condensation, but in other cases a feebly alkaline solution only was required; at the same time an excess of one molecule did no harm and somewhat shortened the time needed to complete the reaction. In the case of the dibenzyl ketone the reaction ran so slowly in aqueous solution that dilute alcohol was taken as the solvent. In each case the condensation seemed to take place most smoothly in the cold; while heat naturally hastened the reaction, the product was then dark colored and the yield diminished. At ordinary temperatures the decomposition was essentially completed in the course of twenty-four or at most forty-eight hours, and so large a product was obtained in each case that the reaction might fairly be called quantitative.

The structure of the bodies prepared from nitromalonic aldehyde by condensation was so well established by the mode of their formation,



that no especial effort was made to obtain confirmatory evidence as to their constitution. At the same time a certain amount of such evidence was collected in the course of the work. From methylethyl ketone a nitrocresol was obtained

which melted at  $94-95^{\circ}$  and which was apparently identical with the (*a*) *m*-nitroorthocresol of Nevile and Winther<sup>1</sup> melting at this point. It gave, on reduction, an amidocresol which melted at  $172^{\circ}-173^{\circ}$  (uncorr.) and this in turn gave toluquinone on oxidation. According to Nölting and Kohn<sup>2</sup> the (*a*) *m*-amidoorthocresol melts at  $172^{\circ}-173^{\circ}$ . The nitrosalicylic which was obtained from acetic ester melted at  $228^{\circ}$  and was therefore the (*a*) *m*-nitrosalicylic acid the structure of which was established by Hübner.<sup>3</sup> The dibasic acid formed from acetone dicarboxylic acid must have its carboxyls adjacent to the hydroxyl with the nitro group in the para place. Through the action of fuming nitric acid it was converted, as is also the (*a*) *m*-nitrosalicylic acid, into picric acid (2, 4, 6-trinitrophenol.)

The diphenylnitrophenol formed from dibenzyl ketone could be converted into the corresponding quinone by successive reduction and oxidation; the para relation of the nitro and the hydroxyl groups was thus established but no additional evidence as to the position of the phenyl groups was obtained.

Quite recently Borsche<sup>4</sup> has published an interesting account of his work upon the action of diazobenzol chloride upon an alkaline solution of nitrosophenol. He describes two bodies, which he calls nitrosooxydiphenyl and nitrosooxydiphenyl benzol. While he was unable at the time to prove the structure of the bodies in question, he very properly assumes that they are probably formed by the introduction of the phenyl group in the ortho position to the hydroxyl. He did not succeed in preparing the corresponding nitrophenols by oxidation, but by reduction he obtained the related amidophenols and from them the quinones and the hydroquinones. His description of the latter bodies agrees well with the observations of Soch and Oenslager, although the melting-points which he gives do not agree sharply with their determinations.

<sup>1</sup> Ber. d. chem. Ges., **15**, 2978.

<sup>2</sup> *Ibid.*, **17**, 365.

<sup>3</sup> Ann. Chem. (Liebig), **195**, 1.

<sup>4</sup> Ber. d. chem. Ges., **32**, 2935.

	Borsche.	S. & O. (corr.)
Amidophenol	146°-147°	149°-150°
Quinone	137°-138°	135°-136°
Hydroquinone	177°-178°	179°-180°

In spite of the discrepancies between these two sets of figures, the general agreement is such that one cannot doubt the identity in structure of the two series.

Borsche's paper was unfortunately overlooked at the time of its publication, and in the meantime Mr. W. J. Hale had already prepared from methylbenzyl ketone the *o*-phenyl-*p*-nitrophenol together with the corresponding amidophenol and quinone. These derivatives of diphenyl, which were of interest in that both substituting groups were in the same benzol ring, agree well with the brief description of the similar compounds made from nitrosooxydiphenyl given by Borsche, but his melting-points are in both cases several degrees lower.

#### *Methylethyl Ketone.*

(a) *m*-Nitroorthocresol,  $C_7H_7NO_3$ .—To a saturated aqueous solution of sodium nitromalonic aldehyde rather more than one molecule of methylethyl ketone was added, and the solution was then made alkaline by the addition of sodic hydrate. An orange-yellow color was rapidly developed, but, if the amount of sodic hydrate added was small (0.2 molecule), no precipitate was formed. After standing in the cold for 24 hours the reaction was apparently at an end and hydrochloric acid then threw down an oil, which gradually solidified as the excess of the ketone evaporated. The weight of the crude product thus obtained was 88 per cent of the theoretical amount of the nitrocresol which should be formed from the sodium nitromalonic aldehyde taken. It melted at 90°-91°, but this melting-point could easily be raised by recrystallization from ligroin, or from a mixture of ether and ligroin, until it reached 94°-95° (uncorr.). Analysis then showed that the body had the composition of a nitrocresol.

0.1363 gram substance dried *in vacuo* over sulphuric acid gave 0.2710 gram  $CO_2$  and 0.0620 gram  $H_2O$ .



	Calculated for $C_7H_7NO_3$	Found.
C	54.88	54.24
H	4.61	5.09

This nitrocresol was readily soluble in alcohol, ether, chloroform or benzol, but more sparingly soluble in ligroin. Its sodium salt was readily soluble in water, but separated from its aqueous solution on the addition of sodic hydrate in slender orange-yellow needles. Its melting-point,  $94^{\circ}$ – $95^{\circ}$  (uncorr.), corresponds exactly with that given by Neville and Winther<sup>1</sup>  $94^{\circ}.6$ – $95^{\circ}$ , for their (*a*) *m*-nitroorthocresol. In order to prove the identity a little more rigorously it was reduced with tin and hydrochloric acid, and the amidocresol precipitated from the solution of the hydrochloride, after the removal of the tin, by the addition of sodic carbonate. The melting-point of the substance purified by recrystallization from benzol proved to be  $172^{\circ}$ – $173^{\circ}$  (uncorr.) in precise agreement with the point given by Nölting and Kohn<sup>2</sup> for (*a*) *m*-amidoorthocresol purified in the same way. On oxidation with sulphuric acid and potassic dichromate in the usual way it gave toluquinone melting at  $67^{\circ}$ – $68^{\circ}$  (corr.).

#### *Dibenzyl Ketone.*

*2,6-Diphenyl-4-nitrophenol*,  $C_{18}H_{13}NO_3$ .—Dibenzyl ketone reacts with sodium nitromalonic aldehyde in slightly alkaline aqueous solution, but the ketone is so slightly soluble in water that the progress of the reaction is extremely slow. Even with dilute alcohol as a solvent the reaction runs slowly, if but a small amount (0.25 molecule) of sodic hydrate is used. It is, therefore, more convenient to dissolve the ketone in four times its weight of alcohol, to add 2 molecules of sodic hydrate in normal solution and then the equivalent amount of sodium nitromalonic aldehyde. A great part of the dibenzyl ketone is precipitated by the dilution of its alcoholic solution with the aqueous sodic hydrate, but, if the whole is constantly shaken, it gradually goes into solution, and at the end of a few hours it has disappeared. The deep orange-red solution is allowed to stand over night in order

<sup>1</sup> Ber. d. chem. Ges., **15**, 2978.

<sup>2</sup> *Ibid.*, **17**, 365.

to complete the reaction, and the alcohol then driven off upon the water-bath. Even after the addition of water to restore the original volume of the solution a large amount of a deep red sodium salt separates. Hydrochloric acid throws down a viscous mass, which gradually hardens, and may then be recrystallized from alcohol. If, however, carbonic dioxide is passed into the solution the crystalline sodium salt gradually disappears as the excess of sodic hydrate is neutralized and crystals of the new nitrophenol begin to take their place. As soon as the liquid is saturated with carbonic dioxide the heavy crystalline precipitate is collected upon a filter and washed with cold water until the wash-water is no longer colored. In this way 94.5 per cent of the theoretical yield of the phenol may be obtained, and in such a pure condition that recrystallization fails to raise its melting-point materially.

0.1577 gram substance dried at  $100^{\circ}$  gave 0.4282 gram  $\text{CO}_2$  and 0.0703 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{18}\text{H}_{13}\text{NO}_5$ .	Found.
C	74.20	74.06
H	4.50	4.99

The 2,6-diphenyl-4-nitrophenol is readily soluble in ether, chloroform, or benzol, but is sparingly soluble in ligroin. It dissolves freely in boiling alcohol, but as the solution cools the greater part separates in flat, obliquely truncated prisms, which usually collect together in the form of leafy aggregations. It melts at  $135^{\circ}$ – $136^{\circ}$  (corr.).

*Potassic 2,6-diphenyl-4-nitrophenylate*,  $\text{C}_{18}\text{H}_{12}\text{NO}_5\text{K} \cdot \text{H}_2\text{O}$ .—

The potassium salt is sparingly soluble in cold water, more readily soluble in hot water, and dissolves readily in alcohol; it may conveniently be recrystallized from dilute alcohol. It forms short yellow needles, which contain one molecule of water of crystallization. They lose this molecule of water slowly over sulphuric acid, more rapidly at  $100^{\circ}$ , and at the same time change their color to a brilliant red.

0.4589 gram salt lost at  $100^{\circ}$  0.0264 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{18}\text{H}_{12}\text{NO}_5\text{K} \cdot \text{H}_2\text{O}$ .	Found.
$\text{H}_2\text{O}$	5.19	5.75

- I. 0.2041 gram anhydrous salt gave 0.0525 gram  $K_2SO_4$ .  
 II. 0.2058 gram anhydrous salt gave 0.0544 gram  $K_2SO_4$ .

	Calculated for $C_{15}H_{12}NO_3K$ .	I.	Found.	II.
K	11.89	11.55		11.87

*2,6-Diphenyl-4-nitroanisole*,  $C_{19}H_{15}NO_2$ .—This body was made in the usual way by the action of methyl iodide upon the potassium salt. It is readily soluble in chloroform, benzol or carbonic disulphide, more sparingly soluble in ether and very sparingly soluble in boiling alcohol or ligroin. It may most readily be crystallized from alcohol with the addition of a little chloroform, and forms clear, clustered, oblique prisms which melt at  $152^\circ$ – $153^\circ$  (corr.).

0.1433 gram substance gave 0.3900 gram  $CO_2$  and 0.0636 gram  $H_2O$ .

	Calculated for $C_{19}H_{15}NO_3$ .	Found.
C	74.71	74.25
H	4.95	4.97

*2,6-Diphenyl-4-amidophenol*,  $C_{15}H_{11}NO$ .—The nitrophenol is readily reduced by tin and hydrochloric acid, if a little alcohol is at the same time added. The hydrochlorate of the base which is formed is sparingly soluble in cold water, more readily soluble in hot water, but its solubility even in hot water is greatly diminished by the addition of a small percentage of hydrochloric acid. The free base was separated in the usual way by the addition of potassic carbonate, and purified by recrystallization from benzol.

0.1509 gram substance gave 7.8 cc. moist nitrogen at  $28^\circ$  and under a pressure of 743 mm.

	Calculated for $C_{15}H_{11}NO$ .	Found.
N	5.38	5.52

The 2,6-diphenyl-4-amidophenol is readily soluble in alcohol, rather more sparingly soluble in ether, and sparingly soluble even in boiling ligroin. It dissolves readily in hot benzol, and crystallizes as the solution cools in rhombic plates, or commonly in more extended flat, obliquely terminated prisms. When recrystallized from benzol it shows the constant melting-point  $149^\circ$ – $150^\circ$  (corr.). The pure base is

unchanged by tolerably long exposure to the air, but the impure body rapidly turns red.

*a-Diphenylbenzoquinone*,  $C_{18}H_{12}O_2$ .—The diphenylamido-phenol was oxidized with potassic dichromate and sulphuric acid diluted with three times its weight of water. The sulphate of the base proved to be very sparingly soluble in the dilute sulphuric acid, and no oxidation was noticed at ordinary temperatures even after long standing. On warming on the water-bath a slow reaction set in, which was apparently completed after several hours heating. The red crystalline product was then collected upon a filter and well washed with water. The quinone may be purified by recrystallization from 80 per cent acetic acid, or by dissolving it in chloroform, evaporating the filtered solution and recrystallizing the red crystalline residue from alcohol.

I. 0.1494 gram substance gave 0.4518 gram  $CO_2$  and 0.0657 gram  $H_2O$ .

II. 0.1400 gram substance gave 0.4232 gram  $CO_2$  and 0.0605 gram  $H_2O$ .

	Calculated for ( $C_{18}H_{12}O_2$ ) <sub>2</sub> .	I.	Found.	II.
C	83.07	82.49		82.45
H	4.66	4.92		4.83

The 2,6-diphenylbenzoquinone is very readily soluble in chloroform, quite readily soluble in benzol or carbonic disulphide, more sparingly soluble in ether and very sparingly soluble in ligroin. It dissolves with difficulty in boiling alcohol, and crystallizes as the solution cools in long slender needles. Hot glacial acetic acid dissolves it freely and deposits it on cooling, but an 80 per cent acetic acid is a more convenient solvent. When recrystallized from alcohol or from acetic acid it melts at  $135^{\circ}$ – $136^{\circ}$  (corr.), and by sublimation it may be obtained in felted, orange-red needles which melt at the same point. When exposed to direct sunlight the red color soon fades and the melting-point is at the same time materially lowered; this change has not been further studied. With concentrated sulphuric acid it gives a blue green coloration.

(a) *Diphenylhydroquinone*,  $C_{18}H_{14}O_2$ .—Sulphurous dioxide

can not advantageously be used for the reduction of the quinone, on account of its slight solubility in water. With glacial acetic acid and zinc a colorless solution is readily obtained, and the hydroquinone may then be precipitated from the filtered solution by the addition of water.

0.1359 gram substance gave 0.4096 gram  $\text{CO}_2$  and 0.0683 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{18}\text{H}_{14}\text{O}_6$ .	Found.
C	82.43	82.21
H	5.39	5.62

(a)-Diphenylhydroquinone is readily soluble in alcohol or ether, sparingly soluble in hot chloroform or benzol and almost insoluble in water, ligroin, or carbonic disulphide. After several recrystallizations from alcohol it formed clear, clustered, oblique prisms which melted at  $179^\circ\text{--}180^\circ$  (corr.); further crystallization from chloroform, from which it separated in transparent, rectangular plates, failed to raise this melting-point. In alkaline solution it is rapidly oxidized by exposure to the air with the formation of red needles, which are apparently the quinone, but on further oxidation the latter again disappear.

#### Acetacetic Ester.

(a)-*m*-Nitrosalicylic Acid,  $\text{C}_7\text{H}_5\text{NO}_6$ .—Nitromalonic aldehyde condenses easily with acetacetic ester provided that two molecules of sodic hydrate at least are used; the product is then the sparingly soluble basic sodium salt of nitrosalicylic acid. It has not been found possible to form the ester of the nitrosalicylic acid directly by the use of a small amount of sodic hydrate. Apparently the saponification of the acetacetic ester by the second molecule of sodic hydrate<sup>1</sup> precedes the condensation. If acetacetic ester is dissolved in a normal solution of two molecules of sodic hydrate and one molecule of sodium nitromalonic aldehyde is added, the color of the solution soon shows that reaction is taking place, and after the lapse of twenty-four hours the solution has nearly solidified with the separation of the long finely-felted, orange needles of the basic sodium salt. The crude acid which

<sup>1</sup> Ber. d. chem. Ges. **32**, 3390.

separates on the addition of hydrochloric acid amounts to 90 per cent of the theoretical weight, and after recrystallization from hot water it has the melting-point,  $228^{\circ}$ - $229^{\circ}$  (uncorr.), and the other properties of the long-known ( $\alpha$ )-*m*-nitrosalicylic acid.

0.1488 gram substance gave 0.2498 gram  $\text{CO}_2$ , and 0.0420 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_7\text{H}_5\text{NO}_5$ .	Found.
C	45.93	45.78
H	2.75	3.16

On the addition of argentic nitrate to a warm aqueous solution of the free acid the silver salt is at once thrown down. When recrystallized from hot water it forms clustered needles.

0.2698 gram of the salt gave 0.1007 gram silver.

	Calculated for $\text{C}_7\text{H}_4\text{NO}_5\text{Ag}$ .	Found.
Ag	37.21	37.31

#### *Levulinic Acid.*

*5-Nitro-2-oxyphenylacetic Acid*,  $\text{C}_8\text{H}_7\text{NO}_5$ .—Pure levulinic acid was dissolved in a slight excess (1.2 molecules) of normal sodic hydrate and a molecule of sodium nitromalonic aldehyde was then added. The color of the solution soon became a deep orange-yellow, and after standing for twenty-four hours hydrochloric acid threw down nitro-oxyphenylacetic acid in well-formed crystals. The slight excess of sodic hydrate somewhat facilitated the reaction, but was not essential. The weight of the product which separated from the dilute solution amounted to 82 per cent of the theoretical yield; by evaporation or extraction of the mother-liquor with ether an additional amount of a somewhat dark colored acid could be obtained. The analysis of substance recrystallized from hot water and dried at  $100^{\circ}$  gave the following results:

I. 0.1526 gram substance gave 0.2691 gram  $\text{CO}_2$ , and 0.0530 gram  $\text{H}_2\text{O}$ .

II. 0.1892 gram substance gave 0.3368 gram  $\text{CO}_2$ , and 0.0685 gram  $\text{H}_2\text{O}$ .



	Calculated for $C_8H_7NO_5$ .	I.	Found. II.
C	48.71	48.11	48.54
H	3.58	3.89	4.05

The 5-nitro-2-oxyphenylacetic acid is readily soluble in alcohol or ether, but is sparingly soluble in chloroform, benzol, or ligroin. It dissolves very readily in hot water, more sparingly in cold water, and crystallizes as the solution cools in long slender prisms. On rapid heating the acid melts at  $160^{\circ}$ – $162^{\circ}$ , but the melting-point is lowered if the substance is slowly heated. When kept at a temperature of  $148^{\circ}$ – $149^{\circ}$  (corr.) it melted in the course of fifteen minutes. This behavior suggested the probable formation of an anhydride, and the *o*-oxyphenylacetic acid has already been shown by v. Baeyer and Fritsch<sup>1</sup> to pass by distillation into its lactone.

*Lactone of the 5-Nitro-2-oxyphenylacetic Acid*,  $C_8H_5NO_4$ .—If the nitro-oxyphenylacetic acid is melted by prolonged heating at  $148^{\circ}$ – $149^{\circ}$  and the temperature is maintained at this point, it gradually solidifies with the separation of long clear prisms, and is then found to have lost in weight an amount nearly corresponding to one molecule of water.

0.4648 gram acid lost at  $148^{\circ}$  0.0408 gram  $H_2O$ .

	Calculated for $C_8H_7NO_5$ .	Found.
$H_2O$	9.14	8.78

During the long heating there had been a slight loss by sublimation and at the same time a small percentage of the acid had escaped dehydration. While the acid and the anhydride could easily be separated by recrystallization, and the greater part of the highly colored by-product could be removed by treatment with cold acetone, the substance obtained was still highly colored. By sublimation a perfectly colorless product was obtained, but it was difficult to prepare larger quantities of material at ordinary pressures. A more satisfactory yield was obtained by sublimation of the acid in an atmosphere of carbonic dioxide under pressure of 50–60 mm., and at a temperature of  $180^{\circ}$ – $185^{\circ}$ . The acid was then but slightly carbonized, and the lactone sublimed in large, colorless, transparent prisms, or in flat, blade-like forms. The

<sup>1</sup> Ber. d. chem. Ges. 17, 975.

body was then crystallized from glacial acetic acid, since its melting-point could be slightly raised in this way.

0.2204 gram substance gave 0.4328 gram  $\text{CO}_2$  and 0.0682 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_8\text{H}_5\text{NO}_4$	Found.
C	53.60	53.57
H	2.81	3.46

This lactone is very sparingly soluble in alcohol, ether, or ligroin, somewhat more readily soluble in chloroform, quite readily soluble in boiling benzol, and still more readily soluble in boiling acetone. It dissolves freely in hot glacial acetic acid, and most of it separates as the solution cools in the form of irregular, pointed needles. On long heating with water it is gradually converted into the acid. It melts at  $187^\circ$ – $188^\circ$  (corr.). This melting-point is so high as compared with that of the acid that it seemed not improbable that a dimolecular anhydride had been formed. A determination of its molecular weight, however, through the boiling-point of its solution in benzol, showed that it was a lactone of ordinary form. 19.6 grams of benzol were employed with the following results:

Substance.	Elevation.	Molecular weight.
0.0914	0.068	183.1
0.1434	0.107	182.5

The calculated molecular weight for the lactone is 179.

*5-Nitro-2-oxyphenylacetic Ethyl Ester*,  $\text{C}_{10}\text{H}_{11}\text{NO}_5$ .—This ester is formed even by warming an alcoholic solution of the acid, and may be prepared by heating the acid with a 3 per cent solution of hydrochloric acid in absolute alcohol. It dissolves with a yellow color in sodic carbonate, but is hardly attacked by acid sodic carbonate. It is sparingly soluble in ether, more readily soluble in boiling chloroform or benzol and is nearly insoluble in ligroin. From hot alcohol it crystallizes well in clear, flat, pointed prisms, which frequently expand to form six-sided plates. It melts at  $154^\circ$ – $155^\circ$  (corr.).

0.1602 gram substance gave 0.3117 gram  $\text{CO}_2$  and 0.0720 gram  $\text{H}_2\text{O}$ .

	Calculated for $C_{10}H_{11}NO_5$ .	Found.
C	53.31	53.08
H	5.39	5.62

*Acetone Dicarboxylic Acid.*

*2,6-Dicarboxy-4-nitrophenol*,  $C_6H_5NO_7 \cdot H_2O$ .—Acetone dicarboxylic acid condenses rapidly with nitromalonic aldehyde in neutral or feebly alkaline solution, and after the lapse of a few minutes the addition of hydrochloric acid causes the separation of fine silky needles of the nitrooxyisophthalic acid which is thus formed. The acetone dicarboxylic acid used was prepared according to the directions of v. Pechman<sup>1</sup> and recrystallized from warm water. It was dissolved in a slight excess of sodic hydrate, 2.25 molecules, one molecule of sodium nitromalonic aldehyde added and the deep orange-yellow solution sharply acidified with hydrochloric acid after the lapse of twenty-four hours. The weight of the product thus obtained amounted to 90 per cent of the theoretical yield, and it could readily be purified by recrystallization from hot water. The acid then crystallizes in finely felted, colorless needles which contain one molecule of water of crystallization; it slowly loses in weight at  $100^\circ$ , but rapidly at higher temperatures.

1.1890 gram substance lost 0.0882 gram  $H_2O$  at  $100^\circ$ .

	Calculated for $C_8H_5NO_7 \cdot H_2O$ .	Found.
$H_2O$	7.35	7.42

The acid dried at  $100^\circ$  then gave the following results:

I. 0.2186 gram substance gave 0.3398 gram  $CO_2$  and 0.0537 gram  $H_2O$ .

II. 0.2224 gram substance gave 0.3468 gram  $CO_2$  and 0.0528 gram  $H_2O$ .

III. 0.2288 gram substance gave 13.3 cc. moist nitrogen at  $25^\circ$  and under a pressure of 749 mm.

	Calculated for $C_8H_5NO_7$ .	I	Found. II	III.
C	42.28	42.39	42.53	
H	2.22	2.75	2.66	
N	6.18	....	....	6.53

<sup>1</sup>. Ann. Chem. (Liebig), **261**, 155.

This nitrooxyisophthalic acid is readily soluble in alcohol, sparingly soluble in ether, and almost insoluble in chloroform or benzol; it dissolves freely in hot glacial acetic acid or in hot water. The anhydrous acid melts at  $213^{\circ}$ – $214^{\circ}$  (corr.), the hydrous acid about  $20^{\circ}$  lower, but since the latter begins to lose its water of crystallization at  $100^{\circ}$ , this melting-point can not be sharply determined. The primary sodium salt is nearly colorless, and very sparingly soluble in cold water, though readily soluble in hot water; it crystallizes in slender, felted needles, which may easily be mistaken for the acid. The secondary sodium salt is pale yellow and quite readily soluble in cold water. The tertiary sodium salt is also readily soluble, but is deep orange-yellow in color. The color of the tertiary salt may be used as an indicator in the titration of the acid, as already noted by Schiff<sup>1</sup> in the case of the basic sodium salt of nitrosalicylic acids.

0.2369 gram hydrous acid required 19.40 cc. tenth-normal sodic hydrate.

	Calculated for $C_8H_5NO_7 \cdot H_2O$ .	Found.
2 NaOH	19.33	19.40

When a hot aqueous solution of the acid is added to a hot solution of argentic nitrate a crystalline silver salt is at once thrown down in the form of finely felted, pale yellow needles. When well washed with hot water and dried in a desiccator this proved to have essentially the composition of a secondary silver salt.

0.2708 gram of the salt gave 0.2280 gram AgBr.

	Calculated for $C_8H_5NO_7Ag_2$ .	Found.
Ag	48.95	48.37

When heated with concentrated hydrochloric acid under pressure at  $180^{\circ}$ – $200^{\circ}$  the nitrooxyisophthalic acid was slowly broken up. Carbonic dioxide was formed, but it was not found practicable, at least on a small scale, to isolate among the products formed the corresponding nitrosalicylic acid. Fuming nitric acid, however, attacked the acid at  $100^{\circ}$  with the evolution of carbonic dioxide. On evaporation and recrystallization of the residue from hot water, picric acid was

<sup>1</sup> Ann. Chem. (Liebig), 198, 265.

obtained in abundance; it melted at  $121^{\circ}$ – $122^{\circ}$  and gave the characteristic potassium salt. Evidently the two carboxyls had thus been directly replaced by nitro groups.

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### CXX.—FERROUS IODIDE<sup>1</sup>.

BY C. LORING JACKSON AND I. H. DERBY.

The accounts of anhydrous ferrous iodide which we have been able to find in the chemical literature are very contradictory. Serullas<sup>2</sup> seems to have been the first to obtain it by the rather strange method of passing iodine and steam through a red-hot iron tube filled with charcoal. He describes it as shining yellow crystals looking like gold filings. Gay Lussac and Davy<sup>3</sup> say it is a brown mass which fuses at a red heat and sublimes at a higher temperature. A. T. Thomson<sup>4</sup> treated one part of iron with two of iodine suspended in water, and after evaporating off the water in a flask containing some free iron, obtained a steel gray laminated mass melting at  $177^{\circ}$  and possessing a sharp puckery taste. When heated in air it left a residue of ferric oxide. In 1861 Carius and Wanklyn<sup>4</sup> prepared it as a gray laminated mass by heating iron filings and iodine in a porcelain crucible. In 1863 De Luca<sup>5</sup> states that Faville had made it under his direction, and that it is a pure white amorphous powder. He gives no statement of the method of preparation in any of the journals which are accessible to us. Finally Erdmann<sup>6</sup> in his *Lehrbuch* (1898) describes it as a reddish-brown body, also without giving the method of preparation. The color of ferrous iodide, therefore, is not by any means settled, the balance of evidence in the chemical literature being in favor of gray or white; but as no analyses of the anhydrous salt have been published, so far as we can find, none of the statements quoted above can be considered to rest on a solid foundation. Under these circumstances it seemed worth while to take up the

<sup>1</sup> Presented to the American Academy of Arts and Sciences, May 10, 1899.

<sup>2</sup> Gmelin-Kraut, *Handbuch*, III, 350, 6th edition.

<sup>3</sup> *Pharm. J.*, **1**, 44 (1842).

<sup>4</sup> *Ann. Chem. (Liebig)*, **120**, 69.

<sup>5</sup> *Compt. rend.*, **55**, 615.

<sup>6</sup> *Lehrbuch der anorganischen Chemie*. 62.

study of ferrous iodide and the results of our work in this field are contained in the following paper.

*Preparation of ferrous Iodide.*

The method adopted consisted in passing the vapor of iodine over heated iron. In the first experiments a combustion tube was used with a stream of carbonic dioxide to carry the iodine, but as we found a temperature above the softening point of hard glass was necessary, we replaced the glass tube with one of iron, which we heated with a Fletcher's tube furnace. At the high temperature thus obtained the iron was oxidized by the carbonic dioxide, and the film of oxide thus formed protected the metal from the action of the iodine; accordingly the carbonic dioxide was replaced by nitrogen, after which good results were obtained.

The apparatus in its final form consisted of two large bottles, which served as gas holders for the nitrogen, and were united by glass tubes and rubber connectors in such a way that, by letting in water from the water works, the gas could be forced out of one of them at a regulated rate through the purifiers and the iron tube to the other bottle, in which it was collected. When this was full of gas, by a simple rearrangement of the pinch-cocks the nitrogen could be forced back through the apparatus again in the same direction as before into the first bottle. By means of this device the same nitrogen could be used over and over again, thus causing a great saving in time and labor. The nitrogen was made by the excellent method of Dr. Gibbs,<sup>1</sup>—equal parts of sodic nitrite, ammonic nitrate, and potassic dichromate were pulverized, and mixed with three parts of water in a flask with a wide delivery tube. The gas came off when the mixture was gently warmed. Twenty-four grams of the mixture gave about 1200 cc., of nitrogen. The nitrogen, after leaving the gas holder, was purified by passing through a solution of sodic hydrate, sulphuric acid, and a long column of calcic chloride, after which the oxygen was removed by means of a layer of finely divided copper heated in a tube of hard glass by means of a kerosene stove. This precaution was necessary, as the nitrogen was

<sup>1</sup> Ber. d. chem. Ges., 10, 1387.



contaminated with air introduced when the tubes were opened, or from the water in the gas holders. We tried at first an alkaline solution of pyrogallol for the removal of the oxygen, but as we found this was not efficient, we resorted to the layer of finely divided copper, which was prepared by reducing cupric oxide.

The reaction took place in three steel bicycle tubes, the largest of which was one inch (2.54 cm.) in outside diameter and about one-sixteenth of an inch (1.59 mm.) thick. The other tubes were somewhat thinner and small enough to slip tightly into the larger tube. The larger tube contained the iron, which was used in the form of wire clippings (card teeth), as it was found by experiment that these gave a better yield of iodide than turnings, filings, or iron by hydrogen. The iron was freed from organic matter by heating it in a stream of hydrogen before using it. The layer of iron in the tube was about 23 cm. long, and this portion of the tube was heated directly by the Fletcher furnace to a bright red heat. One of the smaller tubes was slipped into the larger one at its end nearest the gas holder containing the nitrogen, in this was placed the iodine, which was slowly volatilized by the heat conducted along the iron tube, and the vapor thus formed was swept over the hot iron in the furnace by the stream of nitrogen; this tube was connected with the purifiers by a perforated cork and glass tube far enough from the heat to avoid danger of burning. It was found wise to protect this cork from the iodine vapor, some of which crept back even against the current, by an asbestos or iron diaphragm. The second smaller iron tube was slipped into the further end of the larger tube, and reached the heated portion of it, so that the vapor of ferrous iodide formed in the larger tube condensed in the smaller one, from which it could be easily collected by withdrawing this smaller tube after it had cooled in the atmosphere of nitrogen. The joints of the iron tubes were rendered air tight by means of large rubber connectors, which were kept cool by winding them with lamp-wicking that dipped into a beaker of water. The receiving tube just described was connected with some bottles of strong sulphuric acid to prevent the creeping back of any aqueous vapor into

the tube. The delivery tube from these bottles conveyed the nitrogen to one of the gas holders already described.

In carrying on the process it was observed that a considerable amount of iodine was taken up by the iron before any iodide distilled over; but after it began to appear, it continued to collect for several hours, so that the yield was a good one, and when the apparatus has been once set up the ferrous iodide can be obtained in quantity with little trouble.

As the product of the reaction just described had a deep red color in thin plates, and looked almost black when the mass was even moderately thick, we supposed at first that it could not be a ferrous salt, and accordingly applied the following tests. A little of it treated with water, in which it dissolved completely and with great ease, gave no color with a solution of potassic sulphocyanate, but a strong test for a ferrous salt with potassic ferricyanide. As it was possible that it might be a ferric iodide which was decomposed by water into the ferrous salt and free iodine, we next tested for iodine both with starch paste and with carbonic disulphide, but with negative results. These qualitative experiments indicated that the substance, in spite of its red color, was ferrous iodide; and that this is the case was proved by the following analyses. The substances used in I.-V. and in IX. and X. were the direct product of the reaction. In VI., VII., and VIII., this product had been purified by sublimation before it was analyzed.

I. 0.6717 gram of substance gave 1.0202 gram of AgI and 0.1720 gram of  $\text{Fe}_2\text{O}_3$ .

II. 1.0400 gram of substance gave 1.5736 gram of AgI.

III. 0.9658 gram of substance gave 1.4601 gram of AgI.

IV. 0.7493 gram of substance gave 1.1471 gram of AgI and 0.1934 gram of  $\text{Fe}_2\text{O}_3$ .

V. 0.8327 gram of substance gave 1.2586 gram AgI and 0.2209 gram of  $\text{Fe}_2\text{O}_3$ .

VI. 1.2675 gram of substance gave 1.9232 gram of AgI and 0.3261 gram of  $\text{Fe}_2\text{O}_3$ .

VII. 0.7396 gram of substance gave 1.1192 gram of AgI and 0.1932 gram of  $\text{Fe}_2\text{O}_3$ .

VIII. 0.5944 gram of substance gave 0.8978 gram of AgI.

IX. 0.3831 gram of substance gave by ignition 0.0982 gram of  $\text{Fe}_2\text{O}_3$ .

X. 1.7526 gram of substance gave by ignition 0.4658 gram of  $\text{Fe}_2\text{O}_3$ .

Calculated for					Found						
	FeI <sub>2</sub>	I.	II.	III.	IV.	V.	VI.	VII	VIII.	IX.	X.
I	81.92	82.10	81.77	81.74	82.71	81.66	82.00	81.76	81.64	....	....
Fe	18.08	17.92	....	....	18.07	18.56	18.01	18.28	....	17.94	18.60

Of these analyses I.—VIII. were made by passing sulphurous anhydride into the aqueous solution to convert any free iodine (formed by the action of air on the solution) into hydriodic acid, and to dissolve the ferric hydrate, if any, formed at the same time as the free iodine; then, after driving off the excess of the sulphurous anhydride, the iodine was precipitated as argentic iodide and the iron as ferric hydrate in the usual way. Analyses IX and X., were made by simple ignition of the ferrous iodide in a porcelain crucible, when it loses all its iodine and is converted into ferric oxide.

*Properties of Ferrous Iodide.*

The anhydrous salt prepared as described above forms plates of a deep full red color with a slight brownish tint. This color is a much more pronounced red than any appearing among the ferric salts with the exception of ferric sulphocyanate. In thicker masses it is nearly or quite black; when melted and allowed to solidify, it forms a blackish-red crystalline mass, which looks brown on a surface of fracture.<sup>1</sup> When the plates are examined under the polarizing microscope, they give evidence that they belong to one of the uniaxial systems, but the outlines of these crystals are so ragged that they furnish no means of deciding to which system they belong. Accordingly some of the plates immersed in ether, in which they dissolve very slowly, were observed under the microscope, when the formation of regular hexagonal holes was observed; there is no doubt, therefore, that the crystals belong to the hexagonal system. If the salt is resublimed

<sup>1</sup> The dark color of the ferrous iodide is not without analogy, as G. P. Baxter has found in this laboratory that ferrous bromide has a dark yellow color with a greenish-brown tinge.

slowly, it can be obtained in broad, thin plates with a brilliant vitreous lustre ; but on one occasion very small yellow plates were formed which called to mind the "gold filings" of Serullas. The melting-point of the substance is given by Thomson at  $177^{\circ}$ ; we have not attempted to determine this point anew, as it seemed to us of little practical value on account of the very deliquescent nature of the salt. If heated to about the fusing point of soft glass in an inert gas it sublimes essentially unaltered. When sublimed in a stream of nitrogen, part of the iodide is deposited in the red plates already described, the rest is carried on further in the tube as a yellow cloud, which deposits a dark reddish-brown amorphous powder ; this is found to be much more susceptible to the action of atmospheric moisture than the red plates, but we think this difference in behavior is due only to the difference in the size of the particles in the two specimens. The sublimation may take place in nitrogen, carbonic dioxide, or even hydrogen, but oxygen must be carefully excluded, as this decomposes the iodide rapidly at not very high temperatures, so that on gently heating a sample of it in a porcelain crucible in a few minutes all the iodine has passed off in violet fumes, and there is left a reddish-brown residue of ferric oxide, which retains the shape of the crystals of the ferrous iodide, and is magnetic. That this latter property was not due to the presence of some magnetic oxide or metallic iron in the residue was proved by dissolving it in hydrochloric acid, when a strong test for ferric chloride, but none whatever for ferrous chloride, was obtained. The iodine is so completely removed by this ignition in air that the process was used as a method of analyzing the ferrous iodide (Analyses IX. and X.). De Luca observed a similar decomposition of his (white) ferrous iodide. The same decomposition of the ferrous iodide by the oxygen of the air takes place slowly at ordinary temperatures ; a specimen of it kept in a good desiccator gives off enough iodine vapor in time to color the air within the desiccator a distinct purple. A sample of the salt was kept in a desiccator over potassic hydrate, to absorb the iodine, for thirteen months, and the decomposition followed by occasional weighings, when it was found that about seven-eighths of the total

loss of iodine, was given off in the first six months, but that even at the end of thirteen months the decomposition was not complete, as the residue still contained a little iodine, and gave tests for both ferrous and ferric compounds. It follows from these observations that the salt should not be allowed to stand even in a desiccator before analysis, but should be analyzed as soon as possible after its preparation.

If the salt is exposed to the atmosphere, it deliquesces quickly to a brown solution. The thinner plates, when kept in a corked flask or a desiccator, behaved in a very striking way; the red plate showed at first a white border around its edge, which gradually spread inward, until the whole plate became white; this change was soon followed by a liberation of iodine, which imparted a gray or even black appearance to the mass. The appearance of the iodine is undoubtedly due to the decomposition by air just described, but the cause of the whitening of the crystals was not so evident. The most obvious theories were, that the white substance was a second modification of the ferrous iodide, or that it was produced by the absorption of water, which might either form enough of the green ferrous iodide containing four molecules of water of crystallization to neutralize optically the red color of the anhydrous salt, or might give a definite compound containing less water of crystallization than the green salt. The idea that the white substance was a second modification gained some support from the observations of Thomson, Carius and Wanklyn, and De Luca, who describe ferrous iodide as white or gray, and also from the fact that the white compound was formed in atmospheres containing very little water, although in none of these cases had moisture been rigorously excluded.

We, therefore, tried a number of experiments to settle this point. In all these it was necessary to select specimens of the salt which show this change from red to white, such as rather thin red plates or the brown amorphous powder obtained by sublimation, since thicker plates or masses of the iodide show the phenomenon with difficulty or not at all. We see no reason, however, to ascribe these differences in behavior to anything except the size of the crystals. Two similar portions of the ferrous iodide were exposed, the one to dry

carbonic dioxide, the other to moist carbonic dioxide, the experiments being carried on at the same time and under parallel conditions. The specimen in the moist gas turned white quickly, while that in the dry gas remained unaltered. Other similar experiments showed that the change of color took place much more slowly in a gas containing little moisture than in one containing more. In all these experiments the amount of moisture must be kept small, as, if too much aqueous vapor is used, the salt deliquesces so rapidly that the formation of the white body cannot be observed. A sample of ferrous iodide was immersed in absolute ether (dried with sodium) and underwent no change of color even after long standing; when, however, a minute fraction of a drop of water was added, it rapidly turned white. Upon heating a specimen of the white body in a tube filled with dry carbonic dioxide a cloud appeared which looked like moisture and condensed in the cold part of the tube, the substance turning red at the same time. As the tube cooled this moisture was quickly reabsorbed, and the white body was formed again. This experiment was repeated several times with the same specimen. These experiments leave no doubt that the white substance is not a second isomeric modification of the ferrous iodide, but is formed by the action of water on the red anhydrous salt.

The question next arises, is the white body a mixture of the red anhydrous and the green hydrous ferrous iodide, or is it a crystallized salt with a definite amount of water? Our experiments are not sufficiently conclusive to answer this question with certainty, but we would present the following argument in favor of the second view with all necessary reserve. A sample of ferrous iodide was exposed at ordinary temperatures (in this case about  $22^{\circ}$ ) to an atmosphere of hydrogen kept moist by contact with dilute sulphuric acid containing 33 per cent of acid, and the absorption of water followed by successive weighings at intervals of about a day. Upon plotting these results a curve was obtained, which showed a change in the rate of absorption at a certain point, and a calculation of the amount of water absorbed at this point gave the following result:

0.4289 gram of ferrous iodide absorbed 0.0491 gram of water.

	Calculated for $\text{FeI}_2 \cdot 2\text{H}_2\text{O}$ .	Found.
$\text{H}_2\text{O}$	10.40	10.28

The coincidence of these numbers is certainly striking, and, so far as it goes, tells in favor of a definite composition for the white body; but little weight can be given to a single determination, and in this case the result must be regarded with the more suspicion, because the ferrous iodide, after it had turned from red to white in this experiment, became gray from decomposition with liberation of iodine.

When one of the red plates was viewed under the polarizing microscope in ordinary air, it appeared at first granular and then white, at the same time assuming a lower order of symmetry, as extinction was observed at certain angles when the stage was rotated, an effect which could not have been produced by the original crystal, as it was a hexagonal plate bounded by two basal planes. This observation shows little more than that the white substance was crystalline.

The anhydrous ferrous iodide dissolves rapidly and freely in water with a considerable evolution of heat. The dilute solutions are colorless, the stronger ones green. The hot saturated solutions deposit green crystals of  $\text{FeI}_4 \cdot 4\text{H}_2\text{O}$ . Our analysis of this salt gave results which agreed only approximately with those required by the theory, but this is not strange, as it is very deliquescent and rapidly decomposed by the oxygen of the air with liberation of iodine. The water cannot be determined by loss, as the salt gives off hydriodic acid when it is heated. Fortunately it was not necessary for us to spend our time in attempting to obtain better analytical results, as Volkmann<sup>1</sup> has made a careful study of crystallized ferrous iodide, and has isolated it with four, six, or nine molecules of water of crystallization. From his description of the preparation of these salts there can be no question that the salt obtained by us was  $\text{FeI}_4 \cdot 4\text{H}_2\text{O}$ .

The solution of ferrous iodide, when exposed to the air, is decomposed, turning at first brown and then throwing down a yellowish-brown precipitate of ferric hydrate or a basic

<sup>1</sup> Ber. d. chem. Ges., 27, R. 618.

ferric salt ; iodine is set free at the same time, and apparently some hydriodic acid is also formed.

The ferrous iodide is very susceptible to the action of oxidizing agents, as appears from the account given above of the action of air on it at ordinary temperatures, but it shows a very striking resistance to the action of reducing agents. Its behavior in this respect was studied with some care in the hope of perhaps encountering a subiodide. As has been already stated, ferrous iodide can be sublimed essentially unaltered in an atmosphere of dry hydrogen. This is not perhaps altogether unexpected, as it has been found in this laboratory that cobaltous bromide is only partially reduced when heated in dry hydrogen, the remainder subliming unaltered, while nickelous bromide was reduced under the same conditions essentially without sublimation.<sup>1</sup> When hydrogen was passed through melted ferrous iodide, no more reduction was obtained. Ferrous iodide, sublimed through a layer of iron by hydrogen, remained unaltered. Mercury alone or when emulsified by grinding with diatomaceous earth produced no effect on ferrous iodide even when distilled with it. When melted with molecular silver, on the other hand, the reduction to metallic iron was complete. Reductions in the moist way with hydriodic acid and iron by hydrogen or zinc dust also seemed to give negative results.

C. Liebermann and H. Sachse,<sup>2</sup> and also P. Bruck,<sup>3</sup> have recommended ferrous iodide as a useful carrier in adding iodine to derivatives of acetylene, such as phenylpropionic acid, acetylenedicarboxylic acid, or propargylic acid. We have also tried some experiments on the behavior of ferrous iodide with organic compounds, but as the results are of little interest, we shall summarize them as briefly as possible. Ferrous iodide, when heated to redness in ethylene, was reduced, leaving a magnetic residue containing carbon. With acetylene a very gentle heat was sufficient to start a reaction, which afterward proceeded by itself accompanied by a dull red glow. The products were a volatile, yellow liquid containing much iodine and a voluminous residue consisting

<sup>1</sup> Richards and Baxter : *Proc. Am. Acad.*, **34**, 352.

<sup>2</sup> *Ber. d. chem. Ges.*, **24**, 4112.

<sup>3</sup> *Ibid.*, 4115.



of carbon and very little iron. The fact that the ferrous iodide is reduced by these hydrocarbons, when it is almost unaffected by hydrogen, is remarkable. Isopropyl alcohol heated with ferrous iodide gave a little of an insoluble oil, probably the iodide. When treated with an ethereal solution of aniline, the ferrous iodide formed a white compound much more voluminous than the original salt; this, in all probability, is an aniline addition product analogous to the ammonia compound described later. Benzol, benzyl chloride, ether, phenol, or hydroquinone gave no perceptible action with ferrous iodide.

*Other Methods of Preparing Ferrous Iodide.*

In this section of the paper we shall describe a revision of the methods used by our predecessors, and also some new methods of our own.

The revision of the older methods was necessary, because in three cases the ferrous iodide formed was described as gray or white; and although we have proved that the white samples formed from the red salt owed their change of color to absorption of water, it did not follow that those described by our predecessors were not anhydrous ferrous iodide in a second isomeric form. De Luca,<sup>1</sup> who states that ferrous iodide when pure is white, gives no method of preparation in any of the journals to which we have access, so that it was impossible for us to repeat his work. A. T. Thomson<sup>2</sup> prepared his gray ferrous iodide by evaporating an aqueous solution in a flask containing some free iron. On repeating this experiment we had so much difficulty from oxidation that we carried on our later attempts in an atmosphere of carbonic dioxide. Under these conditions, when the water of crystallization began to come off, the liquid became black and opaque-looking as if it contained a suspended black precipitate. Later the surface of the boiling mass became grayish white with a silvery lustre, but when all the water had been driven off, the residue was brownish-red like the ferrous iodide prepared by our method. This experiment makes it probable that the gray ferrous iodide of Thomson owed its

<sup>1</sup> Comptes rendus, 55, 615.

<sup>2</sup> Gmelin-Kraut: Handbuch, III, 350, 6th edition.

color to the presence of water, for in the absence of analyses he would undoubtedly have ascribed the brownish-red color of the final residue to the formation of a ferric salt by oxidation.

As the method of Carius and Wanklyn<sup>1</sup> consisted in heating iron and iodine in a porcelain crucible, it seemed at first sight that the gray color of the product could hardly be due to the presence of water, and therefore we repeated their work, following their directions as carefully as possible. One gram of rather coarse iron filings,<sup>2</sup> mixed with a little iodine to drive out the air, was heated in a covered porcelain crucible to redness as quickly as possible; four grams of iodine were then added in two portions, and the heating continued until comparatively little iodine vapor escaped around the edges of the cover. When cool, the product was found to be a fused mass, consisting, after it had been broken out of the crucible, of red scales exactly like those described earlier in this paper. These scales upon exposure to the air soon turned grayish-white, and then deliquesced to a brown solution. We have repeated this process of Carius and Wanklyn many times, and in every case the ferrous iodide formed has appeared in red scales, before it had been exposed to the air long enough to absorb moisture. We, therefore, are compelled to ascribe the gray color mentioned by Carius and Wanklyn to the absorption of water from the air, since they, like Thomson, would in the absence of analyses have supposed that the red color was due to oxidation. Our present knowledge, therefore, gives no reason for supposing that anhydrous ferrous iodide has any other color than red.

Another method of preparation may be described here, as it was tried to see whether a white form might not be obtained at comparatively low temperatures. A small quantity of iron by hydrogen was placed in the middle of a small glass tube, and secured by two plugs of asbestos; an excess of iodine was inserted in one end of the tube, which was then filled with nitrogen and sealed at both ends. The end containing the iodine and iron was then heated to 120° by means of an air-

<sup>1</sup> Ann. Chem. (Liebig), 120, 69.

<sup>2</sup> The success of the process depends on using filings of the right degree of coarseness. With too fine or too coarse filings unsatisfactory results are obtained.

bath, and after most of the iodine had sublimed into the cold upper part of the tube, it was reversed so that this end and the iron were heated to  $120^{\circ}$ . After repeating this distillation of the iodine through the iron several times, all the metal was converted into the red ferrous iodide. This is a good method for preparing a specimen to be kept to show the color. Ferrous iodide was also made by passing hydrogen and iodine vapor over heated ferric oxide.

Of these methods of preparation, that of Carius and Wanklyn is the easiest, but it gives a product apt to be contaminated with metallic iron and oxide of iron. Thomson's method is tedious, and does not give a pure product, as we observed evolution of hydriodic acid toward the end of the evaporation even in an atmosphere of carbonic dioxide. The sealed tube method is also slow and imperfect, so that the best method, if the pure salt is desired, is the heating of iron and iodine in nitrogen given in the first part of this paper.

*Action of Ferrous Iodide with Ammonia.*

When anhydrous ferrous iodide was exposed to a stream of ammonia gas at any temperature between  $0^{\circ}$  and  $100^{\circ}$  a large amount of the gas was absorbed, and the iodide was converted into a voluminous white powder. The composition of this substance was determined by finding the increase in weight during the treatment with ammonia.

I. 3.5507 grams  $\text{FeI}_2$ , gained 1.1701 grams of  $\text{NH}_3$ .

II. 2.5411 grams gained 0.8449 gram of ammonia.

	Calculated for $\text{FeI}_2 \cdot 6\text{NH}_3$ .	I.	Found.	II
$\text{NH}_3$	24.76	24.78		24.95

The substance therefore corresponds in formula to the compound  $\text{FeCl}_2 \cdot 6\text{NH}_3$ , made from ferrous chloride under the same conditions.

*Properties of the Hexammonia Ferrous Iodide.*

It forms a pure white amorphous powder, which occupies many times the volume of the ferrous iodide from which it is made, and has a very low specific gravity. Water decomposes it at once with a considerable rise of temperature; the products are ferrous hydrate, ammonic iodide, and ammonia.

We did not succeed in finding an organic solvent for it. When exposed to the air it gives off ammonia rapidly and turns brown; in an atmosphere of ammonia it remains unaltered even at  $100^{\circ}$ ; heated in an indifferent gas it loses ammonia, and is converted into a dark-brown powder, which seems to be stable in the air. Two analyses indicated that this brown substance contained between two and three molecules of ammonia to each molecule of ferrous iodide. Its stability in air leads us to think that it is a new compound, but evidently it was not pure, as the analyses differed by three per cent. Unfortunately we could find no way of purifying it.

*Action of Bromine on Hexammonia Ferrous Iodide.*

When the compound  $\text{FeI}_2 \cdot 6\text{NH}_3$  was exposed to the vapor of bromine, it absorbed a large quantity, so that the product in one case contained 71.03 and in another 70.41 per cent of bromine. This apparent constancy in the amount of bromine absorbed led us to examine the product more carefully in the hope that it might be a definite compound, but our experiments have convinced us that it is only a mixture essentially made up of ferric bromide, ammonic bromide, and an ammonic bromiodobromide,  $\text{NH}_4\text{BrIBr}$ . The product had a reddish-brown color, and gave off bromine when exposed to the air. It was investigated by treating it with ether, in which a portion dissolved with considerable evolution of heat. The residue insoluble in ether had a yellowish color, and seemed to be a mixture of ferric bromide and ammonic bromide in varying proportions. These two substances were recognized by the usual tests. The ether extract on evaporation left a residue which was green with a brilliant metallic luster by reflected light, deep blood-red by transmitted light; it resembled rosaniline, therefore, but the red color was less purplish than in that body. Examined with the microscope, crystals which looked like ammonic bromide were observed. It had a strong odor similar to that of bromide of iodine, and, although not really stable, could be kept for some time without much decomposition. Upon treating it again with ether a fresh quantity of the insoluble yellowish residue was left

behind. The residue obtained by evaporating one of our first ether extracts was analyzed with the following results:

0.7149 gram of the substance gave 0.0216 gram of  $\text{Fe}_2\text{O}_3$ , 0.0405 gram of  $\text{NH}_3$ , and 1.4289 grams of mixed silver salts which yielded 0.7652 gram Ag.

In calculating these results, as the iron from its small amount was evidently an impurity, the amount of ferric bromide corresponding to it has been subtracted from the amount of substance taken, and the bromine contained in this ferric bromide from the bromine found. As the substance gave a test for a ferrous salt, it would have perhaps been more correct to consider the iron present as ferroferric bromide, and this would have given numbers agreeing better with those calculated from the formula; but we think it wiser to give the results on the assumption that ferric bromide was present, and we cannot believe that the amount of ferrous bromide was more than a trace, since the substance had been exposed to an excess of bromine.

	Calculated for $\text{NH}_4\text{BrIBr}$ .	Found. <sup>1</sup>
$\text{NH}_3$	5.90	6.38
I	41.64	40.96
Br	52.46	53.32

These numbers would seem conclusive if it were not for the presence of the small amount of ferric bromide (considered in calculating them) and the appearance under the microscope of crystals resembling ammoniac bromide; but with these sources of error, we thought it necessary to support our analysis with evidence of some other sort, and therefore undertook the preparation of  $\text{NH}_4\text{BrIBr}$  direct in order to compare its properties with those of our compound. Upon treating ammoniac bromide with an ethereal solution of bromine of iodine, the salt dissolved, giving a red solution, and on evaporation of the ether a residue was obtained, the properties of which were identical with those of the ammoniac bromiodobromide described above. Further, upon exposing ammoniac iodide to the vapor of bromine an amount was

<sup>1</sup> If the ferric bromide was not subtracted, the numbers were,  $\text{NH}_3$ , 5.67; iodine, 36.39; and bromine, 56.41.

absorbed corresponding very nearly to that required by the formula.

1.6487 grams of  $\text{NH}_4\text{I}$  absorbed 1.7804 grams of Br.

	Calculated for $\text{NH}_4\text{BrIBr}$ .	Per cent. of bromine. in the product.
Br	52.46	51.92

During the action of the bromine the ammoniac iodide at first turned black, but as the absorption went on it finally became scarlet, and this product proved to be identical with the ammoniac bromiodobromide. A curve constructed from the increase of weight of the ammoniac iodide showed that there was a marked diminution in the speed of the absorption after the first atom of bromine had been added. This decrease in the speed of absorption is undoubtedly connected with the conversion of the black substance into the red  $\text{NH}_4\text{BrIBr}$ , but we are unable to decide whether this black intermediate product is another compound  $\text{NH}_4\text{BrI}$ , or only a mixture of ammoniac bromide and free iodine. It is a curious fact, in view of the absorption of free bromine by ammoniac iodide, that so far as we could find, an ethereal solution of bromine had no action on this salt. We have not continued our experiments in this direction for fear of intruding on the field of work occupied by Wheeler, who with Pratt and Barnes has prepared the ammoniac triiodide.<sup>1</sup>

We have adopted provisionally the name ammoniac bromiodobromide and the formula  $\text{NH}_4\text{BrIBr}$  for this substance, because it is made by the action of bromide of iodine on ammoniac bromide, and when it decomposes bromide of iodine is given off and ammoniac bromide left behind; but we do not feel that these observations settle its constitution finally, although they certainly are strong arguments in favor of the formula adopted. If this is correct, the formation from ammoniac iodide and bromine must be preceded by the replacement of the iodine in the salt by bromine, and this may account for the fact noted above, that an ethereal solution of bromine does not act on ammoniac iodide.

*Properties of Ammoniac Bromiodobromide,  $\text{NH}_4\text{BrIBr}$ .*

The salt has a blood-red color in transmitted light, but is a

<sup>1</sup> This JOURNAL, 19, 675.

brilliant green with a metallic luster by reflected light. The specimens examined by us contained very elaborately twinned crystals with the branches at right angles, but we are inclined to think that these consisted of ammoniac bromide, which is easily formed by the decomposition of our salt; on this account it smells of bromide of iodine, and on long standing leaves a white residue of ammoniac bromide; the same decomposition takes place to a limited extent when it is dissolved in ether; the ethereal solution is dark-red. When treated with water, bromine and iodine are set free, and a solution is formed. Hydrochloric acid sets free, iodine. Sodical hydrate or ammoniac hydrate gives a black precipitate of iodide of nitrogen; upon adding hydrochloric acid to the filtrate from this iodide of nitrogen, bromine is set free. Sulphurous acid gives hydrobromic acid and hydriodic acid.

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Contributions from the Chemical Laboratory of the University of Oregon.

## THE PREPARATION OF ZINC ETHYL.

BY ARTHUR LACHMAN.

About three years<sup>1</sup> ago I published a brief outline of a method of preparing zinc ethyl. As is well known, the chief difficulty in this preparation is to secure a suitable form of zinc; and this difficulty was overcome by the use of zinc dust, which is both cheap and plentiful. My note, though brief, contained all the information needed for the immediate application of the process; and a more detailed description would be entirely unnecessary, were it not that a zinc dust method<sup>2</sup> has since then been published which does not appear to offer any advantages over the older one. The two methods differ in that Simonowitsch uses zinc dust mixed with filings, whereas my process is to be regarded as a modification of the Gladstone-Tribe method<sup>3</sup> in that it uses an alloy of zinc dust with copper. The method of Gladstone and Tribe has long been recognized as yielding by far the best results; and the only obstacle to its universal employment would seem to be the great difficulty of preparing their "zinc-copper couple"

<sup>1</sup> This JOURNAL, 19, 410 (1897.)

<sup>2</sup> Simonowitsch: Chem. Centrbl., 1899, I, 1066.

<sup>3</sup> J. Chem. Soc., 35, 569.

in large quantities. Part of this difficulty lies in the fact that they use zinc filings for this purpose, for filings are hard to procure in quantity; the chief obstacle, however, is that great manual dexterity is required for the successful alloying of the two metals. Moreover, a number of operations are called for: the filings must be freed from oil, they must be cleaned with acid if appreciably oxidized, and then carefully dried, the copper must be prepared by careful reduction of its oxide, and finally the two metals must be alloyed with such care that only small amounts can be taken at one time. As my method yields unlimited quantities of alloy in a single operation which is automatic and does not occupy more than twenty minutes' time, and as it furnishes an excellent yield of zinc ethyl, it may fairly claim to be an improvement upon its progenitor. The details of the new method proposed by Simonowitsch will be considered by the side of the corresponding details of my own.

#### *1. The Zinc Dust-copper Couple.*

Gladstone and Tribe have shown that the best yields are obtained when zinc and copper are alloyed in the proportions of about 9 to 1. Zinc dust contains an average of 90 per cent. of metal, so that the above proportions are approximated if 100 parts of zinc dust are mixed with 12 parts of copper oxide, and then reduced by heating in a current of hydrogen.

100 parts zinc dust and 12 parts copper oxide (in the finest possible powder<sup>1</sup>) are thoroughly mixed and placed in a long glass tube. This tube, which may be of soft glass, should be as wide as the channel of a combustion furnace will permit; at distances corresponding to the length of the channel it should be narrowed to about half its diameter. A plug of glass wool is fitted into one constriction, the tube then filled about one-half full, and a plug inserted into the other end. The tube is now shaken and rotated in a horizontal position until the mixture spreads out in an even layer. A moderate current of dry hydrogen is then passed through the tube, and the latter heated in the furnace. It is not a difficult matter

<sup>1</sup> This is a commercial article.

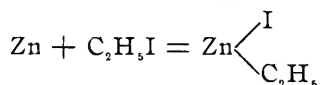


to properly regulate the heating, a flame of about 5 to 10 cm. being needed according to the construction of the furnace. The only essentials are to heat the whole tube at once, to rotate the tube one quarter turn at an interval of a few minutes, and not to be afraid of heating too strongly. It has succeeded best when the powder has slightly baked together, and must be dislodged by a stout wire. Reduction is complete within twenty minutes from the start. The alloy looks much lighter than the mixture and is considerably coarser, though still a fine powder. The contents are allowed to cool in hydrogen (best by removing the tube from the furnace), and are shaken out when no longer hot to the touch. It is advisable to use as soon as possible, though I have kept the alloy several days in an ordinary glass-stoppered bottle without noticeable deterioration.

It will be seen that this method is much more expeditious than the one given by Simonowitsch. The latter first cleans the zinc dust with dilute acid, washes, and finally dries it in a current of carbon dioxide at a definite temperature. This prepared dust must then be mixed with a considerable proportion of dry, clean filings. It has already been pointed out that filings are hard to obtain.

## *2. First Stage of the Zinc Ethyl Synthesis.*

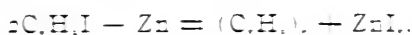
The action of zinc upon ethyl iodide, as is well known, proceeds in two entirely distinct phases. The first consists in a direct addition of ethyl iodide to zinc:



It is carried out at the temperature of the water-bath, and its completion becomes manifest by the disappearance of the ethyl iodide. It is customary to carry out this reaction with a great number of complications, such as a mercury valve for increasing the pressure as well as the boiling-point of the liquid (Simonowitsch uses this device), a current of dry hydrogen for keeping out the air, etc. But these are all unnecessary. Equal parts of alloy and ethyl iodide are simply placed in a flask connected with a long reflux con-

denser, and the mixture kept *gently* boiling on the water-bath until no more ethyl iodide drops back. Violent boiling may drive some of the liquid through the condenser. The time varies from thirty to sixty minutes, according to circumstances that cannot be rigorously defined. I have found it preferable to work with small quantities at a time (from 150-250 grams each of alloy and iodide), to use an Erlenmeyer flask of about 500 cc. capacity, and to take pains to spread the alloy in a thin, even layer on the bottom. The speed of reaction seems to depend on the surface of metal exposed: and this would appear to be the reason why Simonowitsch introduces zinc filings into his flasks.

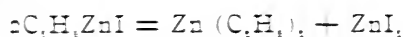
It is a curious fact that the longer the time required for completing this reaction, the more does a secondary process take place, resulting in the formation of butane and consequent loss of zinc ethiodide:



This is an additional reason for desiring rapid action. Once the ethyl iodide is all used up, the process can be indefinitely interrupted at this point, if not convenient to proceed to the final stage.

### 3. *Second Stage of the Synthesis.*

The conversion of zinc ethiodide into zinc ethyl according to the equation:



is accomplished by heating to 180°-220°. The flask containing zinc ethiodide is fitted with a double-bored cork, through which connection is made with a condenser and with a generator furnishing dry carbon dioxide. The current of gas should be moderately rapid at first, very slow during distillation, and rapid again at the end in order to wash out the remaining few cubic centimeters in the flask. The zinc ethyl should be purified by redistillation, as it invariably contains a small amount of unchanged ethyl iodide: for this reason a distilling flask of suitable size should serve as a receiver, to avoid subsequent transfer. The heating is best accomplished

<sup>1</sup> During the boiling little or no liquid penetrates through a thick layer of the powder.

in an oil-bath. In my former note I recommended the use of asbestos air-baths as being cleaner and more expeditious; but this advantage is more than offset by the occasional bursting of a flask at the height of the distillation. Fifteen or twenty minutes suffice for this operation.<sup>1</sup>

The redistillation of zinc ethyl may be conducted with little trouble as follows: The distilling flask is carefully connected with a condenser; the receiver, which should be a stout Erlenmeyer flask, is filled with carbon dioxide, and fitted to the condenser with a cork from which a good-sized wedge has been removed. A current of carbon dioxide is now delivered almost at the surface of the liquid, and continued until all of the air has been expelled from the apparatus. It is desirable to fit the tube into the flask with a cork, and make the gas escape at the receiver. The gas-jet is now replaced with a thermometer already fitted to a cork, and the distillation carried out as with ordinary liquids; a free flame may be used with perfect safety. All flasks to be used as receivers must be filled with carbon dioxide, and fitted with good, sound corks. To change receivers, fasten the carbon dioxide jet used above so as to play a strong current upon the mouth of the first receiver, gently disengage this from the wedge-shaped cork, and then quickly change flasks, *devoting attention primarily to the new receiver*; the old one may be left with impunity for several minutes, if necessary, before being corked.

#### 4. The Preparation of Zinc Ethyl in Quantity.

The process just outlined applies to a single flask of say 200 grams charge, which will yield on an average 60-70 grams zinc ethyl. The time required for all operations except redistillation is at most one and one-half to two hours, usually not much more than one hour. The method is peculiarly advantageous, however, when it is desired to prepare several hundred grams at one time. I have already mentioned that the yields are better if not more than 250 grams be employed in a single operation; but by judicious planning it is not difficult to prepare practically unlimited

<sup>1</sup> The *total* time required is one and one-half hours. Simonowitsch needs two to two and one-half hours, not including the time needed for preparing the metal.

quantities in a single working day. For this purpose select from three to six flasks of the same aperture, so that all fittings shall be interchangeable. Begin operation by preparing a tubeful of alloy (my tube will hold about 350 grams). While this is heating, mount two condensers in connection with water-baths, and prepare the corks. As soon as the alloy is ready, charge two flasks and prepare more alloy. As these processes require almost no attention, employ the interval to fit up the condenser, oil-bath, and fittings for the second heating. As soon as a flask is ready, wipe it dry, and heat in the oil-bath (which may be warmed to about  $110^{\circ}$  or even more); then place a third charge upon the water-bath, etc. By these alternations, little or no time is lost, and employing three condensers as described, about 75 grams per hour will be obtained for each hour after the first (*i. e.*, 75 grams in two hours, 150 grams in three hours, etc.). Of course, any greater number of baths and condensers may be employed, if room and assistance permit. I have always worked alone, and have had plenty of spare time working as above.

### 5. *The Manipulation of Zinc Ethyl.*

The peculiar property possessed by zinc ethyl of rapidly heating itself to the kindling point in air, naturally renders caution necessary when making use of it. In the last few years I have had occasion to handle several kilos of the substance, and have avoided all mishaps by very simple precautions. On the other hand, the very elaborate appliances which have been devised and recommended for this purpose are very likely to deter many from employing this classic synthetic reagent. I may therefore be permitted to summarize my experiences in this direction.

In the first place, all vessels which are to contain zinc ethyl must be filled with dry carbon dioxide. For drying purposes I use a long tube filled with calcium chloride, and two Muencke wash-bottles containing sulphuric acid. The vessels must be kept corked until used. Secondly, as has been demonstrated by Frankland, caoutchouc stoppers and connections must be avoided, and nothing but dry, sound corks

exposed to the vapor of zinc ethyl. Thirdly, the transfer of zinc ethyl is greatly facilitated by pouring it from Erlenmeyer flasks which have perfectly straight sides; and these flasks must be strong enough to withstand sudden and energetic corking. It is inexpedient to attempt the isolation of definite quantities of the reagent; it is much better to pour out the amount needed approximately, and to suit the amounts of other substances to this. The amount taken is given by the loss in weight of the stock vessel; this is not a very accurate procedure, but answers all practical purposes. Fourthly, zinc ethyl may be poured from one vessel to another with perfect safety if the operation is carried out under an inverted funnel of from 4 to 6 inches in diameter, through the stem of which a rapid current of carbon dioxide is passing. After pouring, the first care belongs to the storage vessel; the other readily takes care of itself for some time. This simple expedient does away altogether with the "assistant" usually deemed indispensable when handling zinc ethyl. Finally, everything likely to be needed should be ready in advance, so that no time need be lost. It not infrequently happens that the carbon dioxide generator gives out at a critical moment. I make it an invariable practice to have two on hand, so that the second one may be coupled up without delay.

The chief inconvenience in the preparation of zinc ethyl is the cleaning of apparatus after it is all over. It therefore pays to make up as much as possible at one time. If not needed at once, I keep it in flasks of about 200 cc. capacity, which are about half filled; these are tightly corked, and kept for safety in a large, lead-lined box with metal cover. The substance has been stored this way for months at a time, with no trouble and with practically no loss by oxidation.

#### *6. Experimental Results.*

The following tables will give the data for all the preparations of which I have kept a record; they are not selected, but include the poorest as well as the best I can find in my note-book:

<sup>1</sup> Meyer-Jacobson: "Organic Chemistry," Vol. I, p. 284.

*Velocity of First Stage.*

Amount of each reagent taken, in grams.	Time in minutes for disappearance of ethyl iodide.
150	50
150	48
200	45
300	65
75	30

*Complete Data.*

Iodide used in grams.	No. of separate charges.	Time for completion in hours.	Yield.	Theory.
650	7	4	216	256
300	2	2	95	108
1300	13	10	420	512
500	3	2.5	165	195

These experimental results bear out the claim that the method is quick, certain, and efficient. They correspond to a total yield of 84 per cent in the preparation of nearly one kilogram. It should be remarked that in no case was an attempt made to hurry, and that usually I was at the same time busy with other work.

*7. The Recovery of Iodine.*

The recovery of the iodine which serves as a carrier of energy in this preparation is an exceedingly important affair from the standpoint of laboratory finance. The following method is the one I have found best after many trials:

After heating in the oil-bath, the contents of the flasks form a solid cake. This is broken up with a sharp stick while still warm (it should be remembered that the contents are more valuable than the flask), and dropped into a bucket of water. After standing over night, the liquid is decanted, and the residue washed with water three or four times. A large bulk of liquid is an advantage. The solution is well mixed, and the amount of iodine determined either by analysis or by computation if the quantity of original ethyl iodide is known. After distributing the liquid among several large flasks, which should not be more than half full, add to each the calculated amount of potassium chlorate necessary to free all the iodine, and an excess of commercial hydro-

chloric acid. After an hour or more all the iodine will have settled; if the liquid should grow very warm, which happens when it is too concentrated, cool by standing in water. Decant the acid fluid, wash twice with water, and filter the iodine on a Buchner "nutsche." Press the pulp down hard with a pestle, and draw air through it for several hours.

The iodine thus prepared is by no means dry, but it can be easily used for making ethyl iodide. For this purpose, use as many cubic centimeters of ordinary alcohol as there are grams moist iodine, and take  $1/20$  the weight of the latter of red phosphorus. From 2000 grams iodine I obtained 1720 grams distilled ethyl iodide in this manner. Thus it becomes possible to make a limited quantity of iodine furnish a practically unlimited amount of zinc ethyl.

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## THE USE OF ACETYLENE GAS AS FUEL IN CHEMICAL LABORATORIES.

BY ARTHUR LACHMAN.

Solons who have located so many of our colleges in small towns, far from the highways of civilization, were probably actuated by the best of motives; but it cannot be denied that they have dealt unkindly with the disciples of science, by depriving them of the use of coal-gas. Bunsen's ingenious introduction of this fuel into our laboratories has wrought such a change in experimental methods that the organization of a modern laboratory without a liberal supply of gas would seem an absolute impossibility. And so there have arisen the numerous substitutes which are designed to supply the place of coal-gas. Of these substitutes, it would seem that "gasoline gas" enjoys the greatest popularity. This "gas" is made by simply saturating air with gasoline vapor. For this purpose a variety of contrivances are on the market, the details of which need not be considered here. It is evident at once that such a gas is open to serious objections, the chief of which is the condensation of gasoline in the pipes whenever the temperature sinks appreciably. Another objection is to be found in the comparatively small proportion of vapor to air in this gas; a sample of saturated gas which

I recently analyzed for another purpose, contained only 23 per cent of gasoline vapor ; and in a certain form of machine in common use, the proportion is lowered to 15 per cent, to obviate the condensation above referred to. As a result of this rather attenuated condition of the combustible vapor, it has an unfortunate tendency to blow out at the burners unless both the rate of flow and the pressure are carefully regulated to the construction of the burner.

Our laboratory is supplied with such a tantalizing fuel. In drawing up the plans for a new laboratory building, however, it was found that our machine must be either enlarged or replaced ; and the opportunity was seized to ascertain whether or not acetylene would prove an adequate substitute in point of cost, convenience, and feasibility. I was unable to secure data, either from the current journals or the manufacturers of acetylene burners, relative to other than the mere cost of installation ; and it may therefore be of interest to other isolated chemists to record here the results of my investigations. The data which I have collected may be presented under three heads : (1) The acetylene Bunsen burner ; (2) the properties of the acetylene blue flame ; (3) the comparative operating expenses of acetylene and gasoline gas.

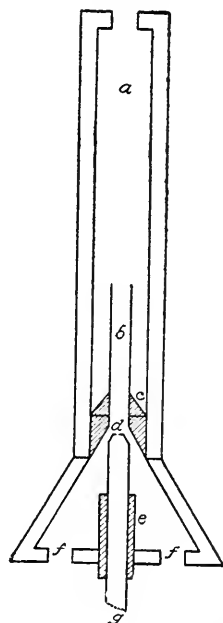
### *1. The Acetylene Bunsen Burner.*

The burners employed in my experiments were kindly supplied by Mr. Breck, Pacific Coast agent of Messrs. Colt & Co., of New York. They are ingeniously constructed of heavy brass, and have certainly solved the problem of furnishing an acetylene flame which does not deposit soot. The essential details of construction are given in the following sketch, which shows the actual dimensions.

The pin-hole supplying gas is very small, and no variations of its orifice are possible ; so that it is quite likely that exposure to laboratory fumes will interfere somewhat with its operation. The burner is supposed to work under a pressure of six inches of water, and at this pressure yields a flame about  $4\frac{1}{2}$  inches high and  $\frac{5}{8}$  inch in diameter. However, it begins to furnish a fairly good flame at a pressure of three inches ; below this the flame becomes luminous.



The burner suffers from a number of defects, which are probably due more to the nature of acetylene than to errors in construction. In the first place, the flame cannot be lowered successfully; the operation requires a very delicate adjustment of the hose-cock, and at best the flame is shortened not more than one inch before it becomes luminous or strikes back. This striking back is the second objection to the burner; for it invariably occurs whenever the gas is turned off. In itself, this would probably not prove objectionable; but it is accompanied by a loud report like the crack of a rifle. It is plain that such a burner would furnish considerable diversion to the average student, and play havoc with the nerves of his instructor. Incidentally, this forcible striking back forms an interesting lecture demonstration of the explosive violence of acetylene-air mixtures; for the total volume of the burner tube is not more than 5 cc.



a. Burner tube; b. Inner mixing tube; c. Cone valve for regulating air supply; d. Pin-hole for admitting acetylene; e. Screw collar for air valve; f. (Four) air-holes; g. Acetylene entrance.

## 2. The Properties of the Acetylene Blue Flame.

It is a trifle incorrect to speak of the acetylene *blue* flame, for the gas burns with a purple color resembling the potassium flame. It cannot therefore be used for flame tests; the color is not absorbed by cobalt glass. Spectroscopic examination revealed the interesting fact that the phenomenon is due to a continuous spectrum, in which red is poorly developed and yellow almost entirely lacking. No lines were observable with my small instrument, even the sodium line being completely absent. The central cone of the acetylene flame is exceedingly small, being not more than  $\frac{3}{16}$  inch high; it has the regular blue-flame appearance, and is very hot (*cf.* below).

Very beautiful effects are obtained if the air-supply is slowly cut off. At first a faint yellow central cone makes its appearance, which then becomes brilliantly white; while at the same time the outer and upper portions of the flame assume a deeper purple tint. Further diminution of air causes a second central cone to envelop the first; it is less lustrous than the latter, and stands out sharply. By very careful manipulation as many as four such cones can be formed within the same flame; and finally the whole jet becomes luminous throughout. The phenomena are well suited to illustrate the theory of combustion within the Bunsen burner.

The acetylene Bunsen flame deposits no trace of soot. However, when it is allowed to play against cooled glass surfaces, a not inconsiderable quantity of colorless oil can be collected. This oil is orthophosphoric acid, shown by its reactions with silver nitrate and with cold molybdate. For use in analytical work, the acetylene must needs be carefully freed from phosphine.

In spite of the high phosphorus content, the burning gas had no determinable effect upon platinum. A piece of very thin foil weighing 0.7 gram was loosely coiled and heated to white heat for over an hour; it had not gained even 1/50 milligram. The same piece was then hung so that its lower edge was bathed by the blue central cone; further heating for an hour and a half did not alter its weight. The phosphine of commercial acetylene would thus seem to have no appreciable action on platinum. The portion of foil which had been hung in the blue flame was etched as if eaten by acid; and at one point two edges had fused together for over  $\frac{1}{4}$  inch. This would indicate a very high temperature in the flame. An additional indication may be found in the much greater luminous intensity of the platinum.

Very intense effects are obtained in the acetylene blast. Using an ordinary Bunsen blast-lamp with foot-bellows, No. 27 platinum wire (diam. 0.33 mm.) melted as easily as in oxyhydrogen. Platinum foil was turned on its edge. In an attempt to use an oxygen-acetylene blast, the blowpipe itself burned away so quickly that the experiment could not be continued. In both cases the flame was white, not colorless.

In spite of the high temperature of the acetylene flame, however, its heating capacity is very small compared with gasoline gas. This is well shown by the following test: A Jena one-liter flask was employed, containing exactly 500 cc. water. The flames were adjusted to play directly against the glass, the distance from burner tip to flask being one-third the height of the full flame. The time was noted from lighting the burner until the water came to boiling:

Acetylene burner No. 1	13 min.
Acetylene burner No. 2	10 "
"Detroit" burner	4½ "

The gasoline burner was an ordinary laboratory specimen, rather below than above the average. It remains to be said in this connection that gasoline and acetylene burners have widely different gas capacities, and that herein lies a partial explanation of this great difference in heating power. This topic will be discussed again below.

### 3. *The Comparative Cost of Acetylene and Gasoline Gas.*

The rate of consumption was measured by noting the fall of a gasometer tank of known capacity. In these tests the above acetylene burners were used, as well as two Detroit burners; the acetylene burners were worked at a pressure of 6 water-inches, the others at the pressure of our gas-machine (1½ inches).

Burner.	I.	II.	III.	IV.
Consumption	0.83	1.0	5.9	4.3
per hour in	0.80	1.0		
cubic feet.				

These figures come very near those claimed by the manufacturers; *viz.*, 1 and 5 feet, respectively.

Carbide is quoted here at about \$6.00 per hundred pounds; gasoline costs about 25 cents per gallon laid down. One hundred pounds of carbide furnish an average yield of 500 feet of acetylene; one gallon 86° gasoline produces about 200 feet of "gas." Per cubic foot acetylene costs 1.20 cents, gasoline gas .0125 cents. Per burner hour the cost becomes: acetylene 1.20 cents, gasoline .0625 cents.

To obtain an adequate idea of the cost of supplying each student with gas during the year, no accurate data are at

hand ; and for my purposes I have assumed that the average student, either elementary or advanced, may be fairly supposed to keep one burner in continual operation each hour he spends in the laboratory. This seems a fair allowance for waste, extravagance, the possession of several burners, and the employment of gas for general purposes (lectures, air-baths, etc.). This assumption has checked with the cost of supplying this laboratory. With an average of thirty-five weeks spent in laboratory work each year, the student will consume for each hour per week in gasoline 22 cents, in acetylene 42 cents. These figures are excessive, owing to the unreasonably high tariffs on the Pacific Coast ; but in all probability the cost of materials is proportionately lower elsewhere. It should be noted, however, that in actual operation acetylene will be at a disadvantage owing to its smaller heating capacity, so that work such as maintaining air-baths at high temperatures, prolonged evaporations, etc., will call for greater expenditure of gas than allowed for here.

#### *4. Conclusions.*

In answer to the question : " Will it pay a laboratory to use acetylene in place of gasoline gas," I think that the foregoing results point to the negative. In many ways, this is to be regretted, as a concentrated, non-condensable gas possesses great advantages over the article in present use. A number of points remain for discussion. The first refers to cost of installation. At first sight, acetylene appears to have the advantage. For equal burner capacity, an acetylene plant is considerably cheaper than a properly equipped gasoline generator. As the gas pipes need have only one-fifth the carrying capacity otherwise called for, a very appreciable saving is effected here also. Against this, however, there is to be set the fact that a purifier which will remove phosphine is absolutely essential. There are no data upon which to base computations of the cost of this operation, but it cannot be very cheap either in installation or in maintenance. Again, even a very large acetylene generator must be cleaned out at least every two weeks, whereas the other machine can run six months without attention. The cost of burners for

either system is about the same ; but a laboratory already well supplied with ordinary burners must purchase a completely new outfit.

Secondly, the difficulties of adjusting the flame of acetylene to small size would preclude its use in all delicate work, such as fractional distillation, thermostat regulation, melting-point determinations, etc. It certainly does not seem practical to have *two* kinds of gas in a laboratory. The use of a small, luminous acetylene jet is out of the question, on account of the inevitable heavy deposit of soot.

The small heat capacity of acetylene, which at first sight seems surprising, is readily explained upon thermochemical data. The comparison must be made between one volume of acetylene and five volumes of "gasoline gas." The latter contains about 20 per cent of vapor, and the vapor, according to some rough experiments I have made, seems to have an average composition of  $C_3H_8$  ; so that we are really comparing equal volumes of acetylene and propane. The heat of combustion of the former is about 3100 K, of the latter 5500 K. The remaining balance in favor of gasoline gas is probably due to the greater surface of contact which its flame presents to the heated objects.

It would thus seem that neither in cost, convenience, nor feasibility can acetylene compete with gasoline as a laboratory fuel. Nor does the future seem likely to bring any adequate change in this matter. Any decrease in the cost of carbide can surely be met by the oil people ; nor are the defects of acetylene as a fuel such as can be remedied by improved burner construction.

EUGENE, OREGON, March, 1900.

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## THE REACTIONS OF ANILINE AND HYDROXYLAMINE WITH HYDROXY- AND UNSATURATED COMPOUNDS.

BY ALFRED TINGLE.

THEORETICAL.

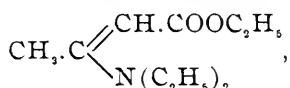
The work of W. Wislicenus<sup>1</sup> and of N. R. Schiff<sup>2</sup> has shown that many so-called  $\beta$ -ketonic esters are in reality mixtures of

<sup>1</sup> Ann. Chem. (Liebig), **291**, 147-216 ; Ber. d. chem. Ges., **32**, 2837-2840.

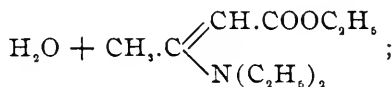
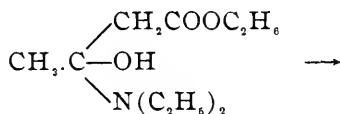
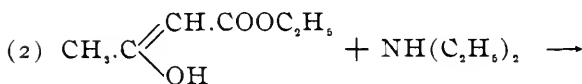
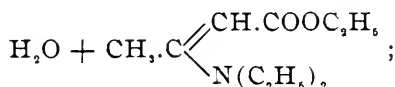
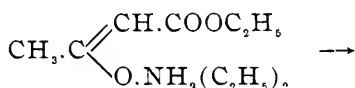
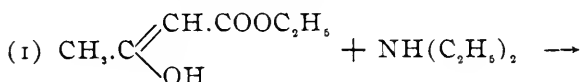
<sup>2</sup> *Ibid.*, **31**, 205-209 ; 601-609.

two substances, one containing the group  $-\text{CO}.\text{CH}_2.\text{COOR}$ , the other the tautomeric form  $-\text{C}(\text{OH}) : \text{CH}.\text{COOR}$ . Whilst these bodies are readily interconvertible, by the action of solvents for example, nevertheless each has, it would seem, a real existence.

Hitherto no attempt appears to have been made to answer the question as to which of the reactions, long recognized as characteristic of the class, are peculiar to the enolic, which to the ketonic form, and which may be considered common to both. For example, Kuckert<sup>1</sup> showed that ethylic acetate and diethylamine give the compound



and believed that it was necessarily produced from the enolic form. It is now seen to be probable that an intermediate compound is formed, and the reaction might take one of the three courses represented below :



<sup>1</sup> Ber. d. chem. Ges., 18, 619.



by examining the reactions of bodies which, whilst containing no double carbon linkage, possess a hydroxyl group, and also one or more highly negative radicals that might render the hydroxyl more active. The reaction (1) above does not depend directly on the double linkage of carbon, and should it really represent the course of events, analogous cases might be encountered. It was also decided to study bodies containing a highly negative group and a double carbon bond, but no hydroxyl. Should addition-products, analogous to the hypothetical intermediate substance in (2), be obtained under these circumstances in any given reaction, we should be justified in believing that the enolic form takes a direct, though perhaps not the whole, part in the corresponding reaction of a ketonic acid. As an example of the first class, ethylic tartrate was selected for preliminary study, while the second class is represented by ethylic cinnamate.

Phenols have also been examined to some extent, but here the case is more uncertain, according to the acceptance or non-acceptance of the Kekulé formula for them. In view, however, of the resemblance pointed out originally by Geuther<sup>1</sup> between ethylic acetoacetate and esters of salicylic acid, it seemed desirable further to investigate the latter with a view of more strict comparison.

Though the results obtained do not, as yet, warrant any decisive conclusion, it is desired to place them on record, whilst the work is continued and extended.

Arppe<sup>2</sup> has shown that when tartaric acid and aniline are heated together at 150° a mixture of tartranilide and tartranil is produced.

In the present investigation ethylic tartrate was employed, and the reaction took a different course. When these substances were brought together under pressure at 100°, in aqueous alcoholic solution, no action could be observed, but on boiling the ester with aniline for somewhat longer than an hour, a mixture was obtained which was extracted with boiling water. Tartranilide, which melts and decomposes at 255°-256°, remained undissolved. On evaporating the aque-

<sup>1</sup> Ann. Chem. (Liebig), **244**, 190-221.

<sup>2</sup> *Ibid.*, **93**, 352-357.



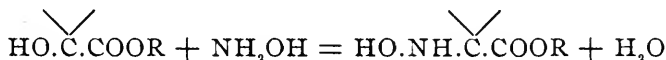
ous extract, a body was deposited which crystallizes in plates and melts, without decomposing, at  $151^{\circ}$ – $152^{\circ}$ . It has the composition  $C_{12}H_{16}NO_6$ , and appears to be ethylic phenyltar-

tramate,  $\begin{array}{c} \text{CHOH.COOC}_2\text{H}_5 \\ | \\ \text{CHOH.CO.NH.C}_6\text{H}_5 \end{array}$ . It is readily soluble in a cold

solution of potassium hydroxide, but less readily so in a solution of sodium carbonate, even when warmed. Grote<sup>1</sup> and Demondesir<sup>2</sup> have shown that tartaric ester reacts in a somewhat similar manner with ammonia. We thus see that, in what may be considered a typical instance, hydroxyl, closely associated with carbonyl groups, but attached to a saturated carbon atom, is inactive towards amines, and not capable of

forming either the group  $\text{R.NH.C}\begin{array}{c} \diagup \\ \diagdown \end{array}\text{CO}$ , or the intermediate compound  $\text{R.NH}\begin{array}{c} \diagup \\ \diagdown \end{array}\text{C}\begin{array}{c} \diagup \\ \diagdown \end{array}\text{CO}$ . *see errata V. 25 p 172*

Several attempts were made to bring about a reaction between ethylic tartrate and hydroxylamine. They were uniformly unsuccessful, and it appears almost certain from these that the reaction



will not take place except in the presence of a double carbon bond. Obviously, however, it would not be safe to consider this conclusion final till many more cases have been investigated.

Some preliminary observations were next made upon the reactions of aniline and hydroxylamine with an unsaturated ester. For this purpose ethylic cinnamate was chosen.

It is conveniently obtained by use of the modification of Fischer's method<sup>3</sup> proposed by J. Bishop Tingle and the writer.<sup>4</sup> The yield is excellent.

On heating ethylic cinnamate with aniline in aqueous-alcoholic solution to  $100^{\circ}$ , under pressure, for four hours, no combination took place. Here we see that aniline is apparently

<sup>1</sup> Ann. Chem. (Liebig), **130**, 203.

<sup>2</sup> *Ibid.*, **80**, 303.

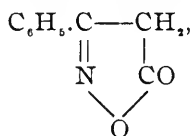
<sup>3</sup> Ber. d. chem. Ges., **28**, 3152.

<sup>4</sup> This JOURNAL, **21**, 243.

incapable of adding itself at a double carbon bond. It is, however, possible that with a more basic amine, or an acid containing a greater number of negative groups, a reaction might occur.

Led by its analogy to sodium camphoroxalate (which readily reacts with amines<sup>1</sup>) an experiment similar to the above was tried, sodium cinnamate being substituted for the ester. No action could, however, be detected.

Thiele and Pickard<sup>2</sup> have examined the action of hydroxylamine on ethylic cinnamate in the presence of sodium ethoxide, and obtained cinnamhydroxamic acid (m. p. 111°.5). The writer's experiments were conducted under very different conditions. Hydroxylamine was liberated from the hydrochloride by an aqueous solution of sodium carbonate, and only enough alcohol was added to bring the ethylic cinnamate into solution. After standing from one to three days, two bodies were found to be produced. The first is an oil, the investigation of which is still incomplete. The second compound crystallizes from dilute alcohol in yellow needles; it is soluble in warm alkalis, and its alcoholic solution gives, with ferric chloride, a brownish color. It melts and evolves gas at 144°.5, and appears to be identical with phenylisoxazolone,



previously obtained by Claisen and Zedel<sup>3</sup> from ethylic benzoylacetate and hydroxylamine. The production of this compound involves a partial oxidation at some point in the reaction, and the exact mechanism cannot be understood till the accompanying product has been more fully investigated; it is clear, however, that the addition of hydroxylamine to the double bond is an essential feature. Such an addition has already been observed in the case of sodium camphoroxalate by J. Bishop Tingle,<sup>4</sup> and of phorone by C. Harries and F. Lehmann.<sup>5</sup>

<sup>1</sup> This JOURNAL, 21, 239; 23, 214-230.

<sup>2</sup> Ann. Chem. (Liebig), 309, 189-205.

<sup>3</sup> Ber. d. chem. Ges., 24, 140.

<sup>4</sup> This JOURNAL, 19, 396.

<sup>5</sup> Ber. d. chem. Ges., 30, 231, 2726.

The oil previously mentioned boiled under reduced pressure at the same temperature as cinnamic ester, but a solid separated from the distillate which melted at  $93^{\circ}$  and was readily soluble in cold water. Potassium hydroxide, even at the ordinary temperature, hydrolyzes the oil to cinnamic acid. On treatment with an alcoholic solution of hydroxylamine at the temperature of the laboratory, it gave phenylisoxazole, and a body which melts at  $65^{\circ}$ – $67^{\circ}$  and is readily soluble in alcohol and chloroform, crystallizing therefrom in plates. When allowed to stand for several days with ethylic acetate, the oil deposited a white solid which melts and decomposes at  $216^{\circ}$ – $217^{\circ}$ .

It was not found possible to bring about any reaction between potassium cinnamate and hydroxylamine.

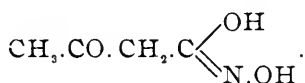
The interaction of hydroxylamine and ethylic cinnamate, and its non-occurrence when ethylic tartrate replaces the latter, points directly to the activity of the enolic, as well as of the ketonic, form of "ketonic" acids when in contact with hydroxylamine, and also shows that this activity is primarily due to the presence of a double carbon bond, and not to the influence of the hydroxyl group.

Geuther<sup>1</sup> insisted on the analogy between the behavior of acetoacetic and salicylic esters, but his argument was chiefly based on the similarity of reaction with potassium hydroxide and carbon dioxide, potassium cyanide, and ferric chloride. There seems to be little analogy in their reactions with hydroxylamine.

Hantzsch<sup>2</sup> showed that when hydroxylamine and ethylic acetoacetate were mixed in alkaline solution, the chief product was

methylisoxazolone,  $\text{CH}_3 \cdot \text{C} \begin{array}{l} \nearrow \text{N}-\text{O} \\ \searrow \text{CH}_2-\text{CO} \end{array}$ , although in presence of

ammonia an unstable compound was formed, which he supposed to be acetoacetylhydroxamic acid,

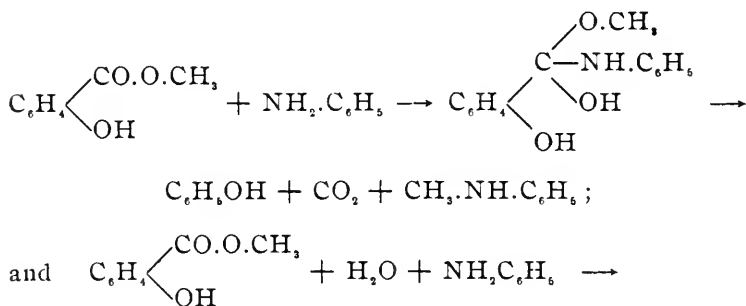


<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Ber. d. chem. Ges.*, **24**, 495-506.

Prior to this, Jeanrenaud<sup>1</sup> stated that methylic salicylate and hydroxylamine give, in alkaline solution, salicylhydroxamic acid. As a doubt of the accuracy of this work has been for some reason expressed by H. Meyer,<sup>2</sup> and as the point seemed to be one of interest, Jeanrenaud's work was repeated. It was found that when methylic salicylate, hydroxylamine hydrochloride and a slight excess of potassium hydroxide were mixed in aqueous alcoholic solution, salicylhydroxamic acid was produced. Its properties were those ascribed to it by Jeanrenaud. No reaction was found to take place between sodium salicylate and hydroxylamine.

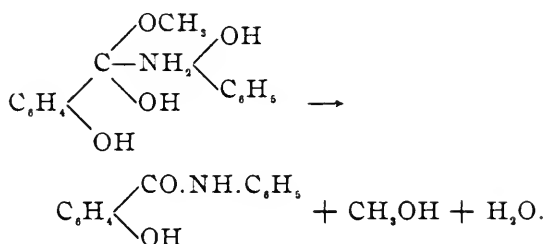
Limpricht<sup>3</sup> has studied the action of aniline upon the monohydroxylbenzoic acids at high temperatures. He found that salicylic acid gave, under these conditions, a small amount of salicylanilide and much phenol. The writer finds that when aniline is boiled with methylic salicylate, both substances being carefully dried before use, the sole products are phenol and methylaniline. When the ordinary amount of hygroscopic moisture was not removed a very small quantity of salicylanilide was formed, but the yield clearly indicated that it was a secondary reaction induced by the presence of water. Methylaniline was identified, as usual, by the formation of methylacetanilide; the yield was very good and it is hoped to extend this reaction to the production of other alkylanilines. The mechanism of the reactions may be represented as follows:



<sup>1</sup> Ber. d. chem. Ges., **22**, 1273.

<sup>2</sup> "Determination of Radicals in Carbon Compounds," American Edition, p. 74.

<sup>3</sup> Ber. d. chem. Ges., **22**, 2907.



Aniline, when boiled with orthonitrophenol for four hours, gives a compound resembling azophenine in its solubilities, appearance, and behavior with concentrated sulphuric acid. It melts sharply, however, at  $201^\circ$ , while the melting-point of azophenine is given as  $241^\circ$ . No analysis has yet been made, as the yield is poor. When paranitrophenol is substituted for the ortho-compound a black amorphous powder is the sole product.

## EXPERIMENTAL.

*Ethylic Tartrate and Aniline.*

These bodies react to produce two compounds, tartranilide, which has already been prepared by Arppe,<sup>1</sup> and a substance which melts, when pure, at  $151^\circ$ – $152^\circ$ . Ethylic tartrate, 5.1 grams (1 mol.), and aniline, 13.9 grams (6 mols.), were boiled together for two hours. The product was then distilled in steam. When the excess of amine had been removed in this manner, the residue in the flask was quickly filtered, tartranilide remaining undissolved in the hot water.

The tartranilide so obtained is pure after a single crystallization from hot alcohol. It was found to melt and decompose at  $255^\circ$ – $256^\circ$ . Arppe merely gives the temperature as "above  $250^\circ$ ." Its properties are identical with those ascribed to it by him; it was further identified by analysis:

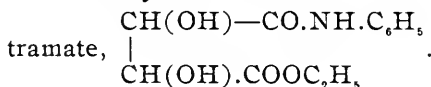
Substance taken, 0.3111 gram;  $\text{CO}_2$  formed, 0.7284 gram;  $\text{H}_2\text{O}$  formed, 0.1562 gram.

	Calculated for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4$	Found.
C	64.00	63.85
H	5.33	5.58

<sup>1</sup> Ann. Chem. (Liebig), 93, 352–357.

The substance which was soluble in hot water was purified by crystallization, first, from dilute alcohol, and finally from water. It was deposited in small white plates and melted, when pure, at  $151^{\circ}$ – $152^{\circ}$ .

The analytical results indicate that it is ethylic phenyltar-



Analysis :

0.2011 gram substance gave 10.7 cc. moist nitrogen at  $25^{\circ}$  and 749 mm.

Substance taken, 0.2084 gram ;  $\text{CO}_2$  formed, 0.4378 gram ;  $\text{H}_2\text{O}$  formed, 0.1150 gram.

	Calculated for $\text{C}_{12}\text{H}_{15}\text{NO}_5$ .	Found.
C	56.91	57.29
H	5.92	6.13
N	5.53	5.92

The compound readily dissolves in a cold solution of potassium hydroxide. It does not dissolve in a cold solution of sodium carbonate, but does so slowly on warming.

#### *Ethylic Tartrate and Hydroxylamine.*

Attempts were made to bring about a reaction between these bodies. Ethylic tartrate was mixed with varying proportions of hydroxylamine hydrochloride in the presence of sodium ethoxide, sodium carbonate, or sodium acetate, and also with an alcoholic solution of free hydroxylamine. In no case was any reaction found to occur.

#### *Preparation of Ethylic Cinnamate.*

E. Fischer's method of esterification, modified according to the suggestion of J. Bishop Tingle and the writer,<sup>1</sup> was employed, and was found to act admirably ; 15 grams of cinnamic acid, boiled for three and a half hours with 100 cc. of 90 per cent alcohol and 7 cc. of concentrated sulphuric acid, gave 15.8 grams of ester, or 91.8 per cent of the theoretical. A comparison was made with the result obtained when using absolute alcohol (2.5 cc. concentrated sulphuric acid to 100 cc. alcohol) ;

<sup>1</sup> This JOURNAL, 21, 243.

it was found that the yield of ester was 98.8 per cent. When working with considerable quantities, however, the loss of ester is unimportant in comparison to the saving in the cost of the alcohol.

*Ethylic Cinnamate and Aniline.*

An attempt was made to obtain an addition-product from equimolecular proportions of ethylic cinnamate and aniline, by heating them at 100° during four hours, under pressure, in the presence of alcohol. No combination, however, occurred. A similarly negative result was obtained when sodium cinnamate was substituted for the ester.

*Ethylic Cinnamate and Hydroxylamine.*

When these substances react upon each other in dilute alcoholic solution, two bodies are formed, the first of which is an uncrystallizable oil which has not yet been thoroughly investigated. The second, a crystalline compound, appears to be identical with Claisen and Zedel's phenylisoxazole.<sup>1</sup> It melts and decomposes at 144°.5.

Hydroxylamine hydrochloride, 20.4 grams (3 mols.), and sodium carbonate, 16.8 grams (1.5 mols.), were mixed in aqueous solution, and ethylic cinnamate, 17.2 grams (1 mol.) added, with sufficient alcohol to dissolve it entirely. The whole was allowed to stand three or more days at the temperature of the laboratory. At the end of that time the greater part of the alcohol was boiled off, water was added, and the oil which separated was extracted with ether. The aqueous layer was next slightly acidified with dilute sulphuric acid, filtered, and again extracted with ether. The substance precipitated was identical with that subsequently obtained on evaporating the ether, the total yield of crude product being 4.5 grams. It was purified by draining on a porous tile and subsequently crystallizing from dilute alcohol.

Analysis:

Substance taken, 0.2490 gram; CO<sub>2</sub> formed, 0.6140 gram; H<sub>2</sub>O formed, 0.1148 gram.

0.1487 gram substance gave 11.5 cc. N at 22° and 740 mm.

<sup>1</sup> Ber. d. chem. Ges., 24, 140.

	Calculated for $C_9H_7NO_2$ .	Found.
C	67.08	67.25
H	4.34	5.12
N	8.69	8.52

Determination of molecular weight.<sup>1</sup>

Value of K for solvent (phenol) = 75.00.

Amount of substance taken. Gram.	$\Delta$ .	Molecular weight.
0.1260	0°.33	143.7
0.2510	0°.70	134.9

Amount of solvent employed, 19.9320 grams.

The compound crystallizes in golden-yellow needles, as described by Claisen and Zedel,<sup>2</sup> who give its melting-point as 147°. Its alcoholic solution gives a brownish coloration with ferric chloride.

#### *Potassium Cinnamate and Hydroxylamine.*

Attempts were made to bring about a reaction between these compounds, in the presence of potassium hydroxide, sodium carbonate, or sodium acetate, both by prolonged action at the temperature of the laboratory and by heating on the water-bath. No success was attained.

#### *Methylic Salicylate and Hydroxylamine.*

The reaction between these substances has already been investigated by Jeanrenaud,<sup>3</sup> but some doubt having been thrown on the results obtained by him, it was considered advisable to reinvestigate the matter. The experimental conditions were slightly changed before obtaining the best results, but the formation of salicylhydroxamic acid was fully confirmed.

Hydroxylamine hydrochloride, 6.9 grams (2 mols.), was mixed, in aqueous solution, with 14 grams (5 mols.) of potassium hydroxide; 7.6 grams (1 mol.) of methylic salicylate were added, with sufficient alcohol to bring the whole into solution. The mixture was allowed to stand at the temperature of the laboratory for two days. A slight excess of dilute

<sup>1</sup> I am indebted for this determination to Mr. R. D. Hall, of this university.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> Ber. d. chem. Ges., 22, 1270-1284.



sulphuric acid was next added, the acid liquid was diluted with water and extracted with ether. The extract, after distilling off the ether, was steamed on the water-bath to remove traces of salicylic acid. In this way a residue of salicyl-hydroxamic acid was obtained. It was recrystallized from alcohol, and, after purification, melted and decomposed at  $171^{\circ}$ .

#### Analysis :

Substance taken, 0.2367 gram ;  $\text{CO}_2$  formed, 0.4727 gram ;  $\text{H}_2\text{O}$  formed, 0.1001 gram.

	Calculated for $\text{C}_7\text{H}_7\text{NO}_2$ .	Found.
C	54.90	54.46
H	4.57	4.69

That a slight departure from the conditions described causes a great difference in the course of the reaction is shown by the following experiment :

The methylic salicylate and hydroxylamine hydrochloride were mixed in the same proportions as before, but only three molecular proportions of sodium hydroxide were added, and a quantity of alcohol insufficient to completely dissolve the ester. The reaction was allowed to continue for sixty-six hours. The only product obtained was salicylic acid. It is possibly through the occurrence of some such variation that doubt has been cast on Jeanrenaud's accuracy.

#### *Sodium Salicylate and Hydroxylamine.*

Attempts to obtain, from sodium salicylate and hydroxylamine, an addition-product, similar to that obtained by J. Bishop Tingle<sup>1</sup> from sodium camphoroxalate and hydroxylamine, were unsuccessful. Salicylic acid was invariably regenerated.

#### *Methylic Salicylate and Aniline.*

The nature of the reaction in this case varies, according to whether hygroscopic moisture is or is not excluded. When the dried substances are boiled together in a carefully dried apparatus the products of the reaction are phenol and methylaniline. The details of the experiment are as follows :

<sup>1</sup> This JOURNAL, 19, 396.

Methylic salicylate, 15.2 grams (1 mol.) dried by means of calcium chloride, was boiled for five hours, in a well-dried reflux apparatus, with 45.5 grams (5 mols.) of aniline dried over sodium. The resulting oil was distilled, leaving only a small quantity of an uncrystallizable tar in the distilling flask. The distillate was shaken with a solution of potassium hydroxide and then extracted with ether. The material soluble in ether boiled between  $180^{\circ}$  and  $186^{\circ}$ , and consisted of a mixture of aniline and methylaniline. These were separated by conversion into their sulphates, that of methylaniline being readily soluble in water. Free methylaniline was subsequently recovered, and was recognized by the formation of methylacetanilide (melting at  $101^{\circ}$ – $103^{\circ}$ ) on treatment with acetyl chloride. The yield of methylaniline by this reaction is good. The alkaline aqueous solution, after the removal of the bases, was acidified with dilute sulphuric acid; oily drops separated; they were identified as phenol by their smell and by the formation of tribromphenol, melting at  $91^{\circ}$ – $92^{\circ}$ .

A series of experiments was also conducted in a similar manner, but without taking any precautions in drying the materials used. Under these circumstances it was found that in addition to methylaniline and phenol, salicylanilide was always formed. This remained behind after distilling off the phenol and mixture of bases. It was drained on tile and it then crystallized from dilute alcohol in warty tufts of needles, melting at  $132^{\circ}$ . Analysis:

Amount of substance taken, 0.2926 gram;  $\text{CO}_2$  formed, 0.7825 gram;  $\text{H}_2\text{O}$  formed, 0.1370 gram.

	Calculated for $\text{C}_{13}\text{H}_{11}\text{O}_2\text{N}$ .	Found.
C	73.23	72.93
H	5.16	5.20

That the formation of salicylanilide is the result only of a secondary reaction is shown by the smallness of the yield. In one experiment 15.2 grams of methylic salicylate and 46.5 grams of aniline were employed: only 0.8 gram of crude salicylanilide was obtained, whilst at the same time 7.4 grams of phenol, and 28.5 grams of the mixed bases were isolated.

Various experiments were made to induce aniline to react

with methylic salicylate at  $100^{\circ}$ , in analogy with the formation of  $\beta$ -anilidocrotonic ester,<sup>1</sup> but these were unsuccessful.

An attempt to cause aniline and sodium salicylate to react in a manner similar to that leading to the formation of phenylcamphoformeneaminecarboxylic acid from camphor-oxalic acid<sup>2</sup> and aniline, was also not successful.

#### *Orthonitrophenol and Aniline.*

*o*-Nitrophenol, 10 grams (1 mol.), was boiled for four hours with 28 grams (4 mols.) of aniline. The resulting mixture was made alkaline and distilled in steam, then made acid, and again distilled in steam. The contents of the distilling-flask were filtered. The insoluble substance thus separated was purified by boiling with alcohol to remove the tar, and crystallized from chloroform. So purified it forms plates having a red-brown color. It melts quite sharply at  $200^{\circ}$ – $201^{\circ}$ . With concentrated sulphuric acid it gives a reddish color when cold, but a clear blue one when strongly heated. It is probably formed by an oxidation-product of the aniline condensing with other aniline molecules. When the heating of aniline and *o*-nitrophenol is long continued only a black uncrystallizable powder is produced.

#### *Paranitrophenol and Aniline.*

These bodies, when boiled together for six hours, yield only a black amorphous powder; there is evidently a difference of a pronounced kind between the actions of these nitrophenols with aniline.

It is hoped in the future to continue and extend this work in various directions.

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<sup>1</sup> Ber. d. chem. Ges., **20**, 944.

<sup>2</sup> This JOURNAL, **21**, 239; **23**, 225.

Contributions from the Sheffield Laboratory of Yale University.

LXXV.—ON THE MOLECULAR REARRANGEMENT  
OF THE THIONCARBAMIC, THIONCARBAN-  
ILIC, AND THIONCARBAZINIC ESTERS:  
 $\beta$ -ALKYL- $\alpha$ - $\mu$ -DIKETOTETRAHY-  
DROTHIAZOLES.

BY HENRY L. WHEELER AND BAYARD BARNES.

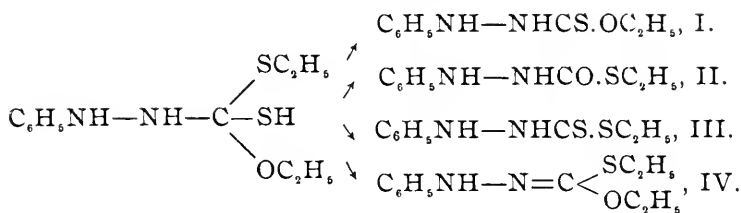
In a recent paper we showed that the thioncarbamic esters,  $H_2NCS.OR$ , undergo a molecular rearrangement in the presence of alkyl halides, with great ease, giving the isomeric thiol compounds,  $H_2NCO.SR$ . In this paper we describe the results of an examination of certain monosubstituted xanthogenamides,  $XNHCS.OR$ , under similar conditions and of the preparation of some homologues of "mustard-oil acetic acid" or  $\alpha$ - $\mu$ -diketotetrahydrothiazole.

We find, when X in the above formula is  $C_6H_5$ —, that these compounds, the thioncarbanilic esters, react less readily than the non-substituted thioncarbamic esters. With methyl and ethyl iodides they require more or less protracted heating, while with isobutyl iodide no rearrangement was observed. In order to extend our knowledge of the thion esters, we examined also the phenylthioncarbazinic esters,  $C_6H_5NH—NHCS.OR$ , in which X is the positive grouping  $C_6H_5NH$ .

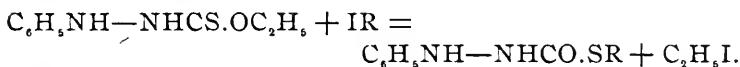
Of the three possible types of phenylthiocarbazinic esters certain dithio<sup>1</sup> and thiol<sup>2</sup> compounds have been described, but methods were lacking for the preparation of the thion derivatives. It seemed probable that these compounds would result by the action of phenylhydrazine on the dithiocarbonic esters, although the reaction, if taking place between equal molecules and if confined to the  $\beta$ -amino group, and excluding tautomeric forms, might still proceed in four different ways, the dithio ester and the phenylhydrazine first combining to form an addition-product, then decomposing as follows; *i. e.*, with the evolution of mercaptan (I. or II.), or alcohol (III.), or hydrogen sulphide (IV.):

<sup>1</sup> Busch: Ber. d. chem. Ges., 28, 2635.

<sup>2</sup> Busch and Stern: J. prakt. Chem., 60, 242.

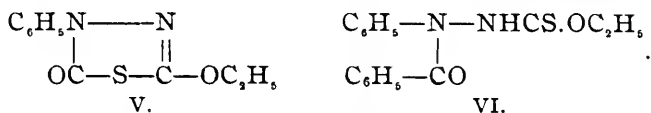


In fact, it was found that this reaction proceeds chiefly in the sense of the first and last representations, a solid and an oil being obtained. The solid material is the phenylthioncarbazinic ester (I.). This reacts readily with methyl iodide, ethyl iodide, benzyl chloride, etc., giving the phenylthiolcarbazinic esters just described by Busch and Stern:<sup>1</sup>



This molecular rearrangement takes place at ordinary temperatures, and, therefore, more readily than in the case of the thioncarbanilic esters, a basic character of the molecules being more favorable for rearrangement than a negative one.

Phenylthioncarbazinicethyl ester (I.), reacts with phosgene in toluene, giving ethoxyphenylthiobiazolone (V.), a representative of a new type of alkyloxythiobiazolones, the other theoretically possible types having been described by Busch. The carbazinic ester reacts with benzoyl chloride, evolving ethyl chloride, but the evolution of this gas is due to a secondary reaction, the chief product obtained being a benzoyl derivative (VI.). The same benzoyl derivative is formed from the sodium salt of the carbazinic ester and benzoyl chloride:



The formula VI. is assigned to the benzoyl compound because it is soluble in alkali and can be precipitated unaltered by acids. That the benzoyl group is not attached to sulphur is shown by the fact that the compound can be boiled with alkali or acids without decomposition.

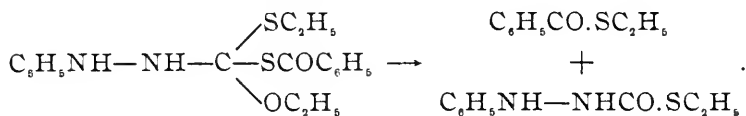
<sup>1</sup> *Loc. cit.*

The action of acyl chlorides is tautomeric when compared with the behavior of the alkali salts of the carbazinic ester with alkyl iodides, for, if phenylthioncarbazinicethyl ester is treated with ethyl iodide in the presence of alcoholic potash the following represents the course of the reaction :



The oil thus obtained being identical in every respect with the hydrazone (IV.), obtained by the direct action of phenylhydrazine on diethyl dithiocarbonate. This behavior is, therefore, similar to that of the thioncarbanilic<sup>1</sup> and the dithiocarbazinic esters,<sup>2</sup> but it differs from that of the oxygen analogues,<sup>3</sup> inasmuch as the latter give nitrogen alkyl derivatives.

When the above hydrazone is treated with thiobenzoic acid a peculiar reaction takes place and phenylthiolcarbazinicethyl ester, (II.), and ethylthiol benzoate are almost quantitatively obtained. The hydrazone and the thio acid combine at the double bond, then separate as follows :



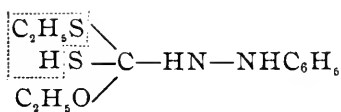
A similar reaction takes place with thioacetic acid. In addition to the above reaction a small amount of hydrogen sulphide is evolved but no acetyl- or benzoylhydrazone was isolated.

The hydrazone can be changed back to the thioncarbazinic ester by passing hydrogen sulphide into the material heated to 125°, or, it can be converted into the thiol ester by treating it with hydrogen chloride in benzene solution. These reactions involve the formation of the following addition-products, which decompose in the two opposite ways, as follows :

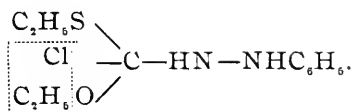
<sup>1</sup> Liebermann : Ann. Chem. (Liebig), **207**, 148; Fromm and Block : Ber. d. chem. Ges., **32**, 2212.

<sup>2</sup> Busch and Lingenbrink : Ber. d. chem. Ges., **32**, 2620.

<sup>3</sup> Hantsch and Mai : *Ibid.*, **28**, 977.



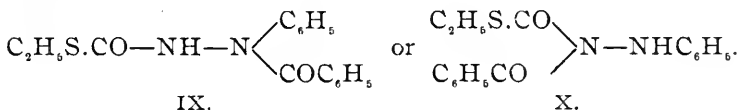
VII.



VIII.

In the case of the action with hydrogen chloride the addition-product (VIII.) was isolated; and in the absence of moisture this is stable at temperatures below  $57^\circ$ .

The hydrazone reacts energetically with acetyl and benzoyl chlorides and in the same manner as in the case of the substituted imidoesters, inasmuch as ethyl chloride is evolved and a N-acyl derivative is formed. That the ethyl group attached to oxygen is the one evolved as ethyl chloride in this reaction, and not the group attached to sulphur, is shown by the fact that on boiling the benzoyl derivative with hydrochloric acid phenylthiolcarbazinicethyl ester, (II.), is obtained. The benzoyl compound, therefore, has one of the following thiol structures :



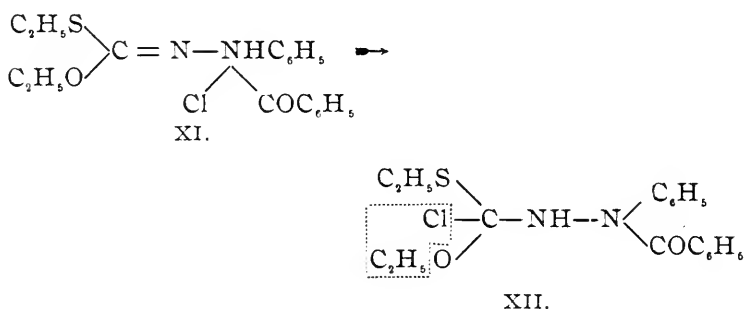
This is confirmed by the fact that the thiol compound,



reacts smoothly with benzoyl chloride, hydrogen chloride being evolved, and the above benzoyl derivative is formed. That the structure represented by formula IX. is probably the correct one, or, in other words, that the acyl groups are in the  $\alpha$ - $\beta$ -positions in respect to each other is shown by the acid properties of the compound; it dissolves in alkalis and can be precipitated, even after boiling, unaltered by acids. Although a diacyl derivative corresponding to the formula X. would be expected to be formed here from analogy with the imido esters. This, however, would probably be insoluble in alkali.

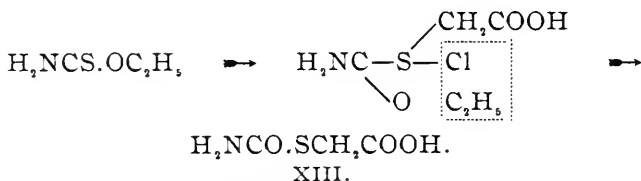
The following, therefore, represents the action of the hydrazone with benzoyl chloride, the addition taking place with the formation of a pentavalent nitrogen product, XI., and not at

the double union as represented in the case of the isoanilides;<sup>1</sup> this product then rearranges with loss of ethyl chloride, as shown in formula XII.:



The thiocarbazinic esters and the hydrazone are very reactive with compounds of a negative character; but, on the other hand, with bases they show little tendency to react.

Libermann and Voltzkow,<sup>2</sup> who investigated the action of chloracetic acid on "phenylsulfurethan," and Langlet,<sup>3</sup> who examined the behavior of xanthogenamide with bromacetic acid and  $\beta$ -iodpropionic acid, represented the amides as acting in the pseudoform, and hydrogen chloride as separating in the first stage of the action. It was suggested, however, by P. Meyer<sup>4</sup> that this reaction probably takes place first with the separation of alkyl halide, and this we find to be the case. For example, chloracetic acid reacts with xanthogenamide at 100° in the same manner as with alkyl halides, and there is no reason for assuming, from this reaction, that the thioncarbamic esters have the pseudoform, the reaction taking place as follows:



<sup>1</sup> Wheeler and Walden: *This JOURNAL*, 19, 130.

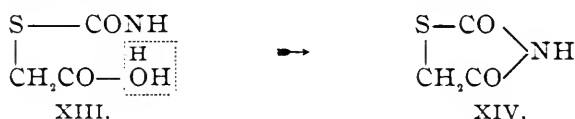
<sup>2</sup> *Ann. Chem. (Liebig)*, 207, 137.

<sup>3</sup> *Ber. d. chem. Ges.*, 24, 3849.

<sup>4</sup> *Ibid.*, 14, 1663.

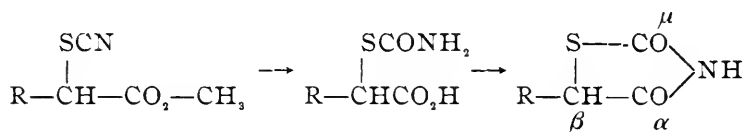


The carbaminthiolglycollic acid, XIII., thus formed, which was isolated, loses water, giving the ring-formed compound,  $\alpha$ - $\mu$ -diketotetrahydrothiazole (Senfölessigsäure).<sup>1</sup>



Since the acids  $\text{XCH}_2\text{COOH}$  and  $\text{XCH}_2\text{CH}_2\text{COOH}$  react readily with xanthogenamide and phenylxanthogenamide, it seemed of interest to determine whether the homologues of the above ring or the  $\beta$ -alkyl derivatives would result in the same manner by employing the halogen acids  $\text{RCHXCOOH}$  and their esters. It is our experience, however, that these latter compounds react by no means as smoothly as the former; at any rate, a large part of the xanthogenamide undergoes a rearrangement into the corresponding thiol ester and decomposition occurs, giving cyanuric acid, thiol acid, and other products.

We find, however, that the  $\alpha$ -sulphocyan derivatives of the fatty acid esters, at least the lower members of the series, are capable of the same transformation under the influence of hydrochloric acid as that observed by Heintz<sup>2</sup> and Claesson<sup>3</sup> in the case of sulphocyanethyl acetate, and that by this means the homologues in question can be prepared. The methyl and ethyl esters give the best yields of the  $\beta$ -alkyl- $\alpha$ - $\mu$ -diketotetrahydrothiazoles, the hydrolysis probably taking place as follows:



#### EXPERIMENTAL PART.

*Phenylthioncarbazinicethyl Ester*,  $\text{C}_6\text{H}_5\text{NH} - \text{NHCS} \cdot \text{OC}_2\text{H}_5$ .  
—115 grams of xanthogenic ester,  $\text{C}_2\text{H}_5\text{SCS} \cdot \text{OC}_2\text{H}_5$ , and 80 grams of phenylhydrazine were warmed for twelve hours on

<sup>1</sup> Compare Hantsch and Aripides: *Ann. Chem. (Liebig)*, **249**, 8.

<sup>2</sup> *Ann. Chem. (Liebig)*, **136**, 232.

<sup>3</sup> *Ber. d. chem. Ges.*, **10**, 1352.

the steam bath when hydrogen sulphide and ethyl mercaptan were evolved, and, on cooling, 77 grams of the carbazinic ester separated. This was filtered on the pump and separated from the hydrazone, which latter, after washing with alkali, was dried at  $100^{\circ}$  in a vacuum, when the oil thus obtained weighed 37 grams.

The carbazinic ester was purified by crystallizing from ligroin or alcohol, from which solvents it separates in the form of needles melting at  $72^{\circ}$ – $74^{\circ}$ . A nitrogen determination then gave:

	Calculated for $C_9H_{12}N_2OS$	Found.
N	14.2	14.1

This compound dissolves in alkali and is precipitated unaltered by acids.

*Phenylthiolcarbazinimethyl Ester*,  $C_6H_5NH-NHCO.SCH_3$ .—This compound was obtained when two grams of the above ethyl ester were dissolved in 5 grams of methyl iodide. On standing for several hours and then evaporating the methyl iodide, colorless needles melting at  $152^{\circ}$  were obtained. In spite of the fact that a nitrogen determination came low (analysis A) this material is identical with that prepared from potassium thiolcarbazinate,  $C_6H_5NH-NHCO.SK$ , and methyl iodide (analysis B) which was first obtained in the latter way by Busch and Stern.<sup>1</sup>

	Calculated for $C_8H_{10}N_2OS$ .	A.	Found. B.
N	15.3	14.7	15.5

*Phenylthiolcarbazinicethyl Ester*,  $C_6H_5NH-NHCO.SC_2H_5$ , when prepared by treating the thioncarbazinic ester or the salt,  $C_6H_5NH-NHCOSK$ , with ethyl iodide, was obtained in needles melting at  $112^{\circ}$ . Busch and Stern give  $113^{\circ}$ . A nitrogen determination gave:

	Calculated for $C_9H_{12}N_2OS$ .	Found.
N	14.2	14.0

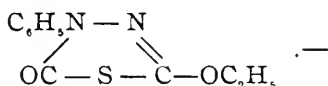
This compound is insoluble in alkali. When this and the preceding compound were heated with molecular proportions of aniline, on the steam-bath, carbanilide was obtained.

<sup>1</sup> Loc. cit.

*Phenylthiolcarbazinibenzyl Ester,*

$C_6H_5NH-NHCO.SCH_2C_6H_5$ .—When 3 grams of the thion ester were heated with 1.9 grams of benzyl chloride on the steam-bath, ethyl chloride was evolved and the mixture soon solidified. On crystallizing then from alcohol, clusters of spears or needles were obtained melting at  $170^\circ$ , as stated by Busch and Stern. A nitrogen determination gave:

	Calculated for $C_{14}H_{14}N_2OS$ .	Found.
N	10.8	10.0

*Ethoxyphenylthiobiazolone,*

5 grams of the thioncarbazinic ester and 13 grams of a 20 per cent solution of phosgene in toluene were heated on the steam-bath for half an hour. On evaporating the solvent in a vacuum, an oil was obtained which finally solidified. The material then crystallized from alcohol in colorless prisms which melted constantly at  $38^\circ$  and a nitrogen determination gave the following result:

	Calculated for $C_{10}H_{10}N_2O_2S$	Found.
N	12.6	12.3

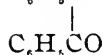
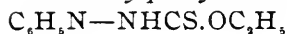
*Phenylthioncarbazinimethyl ester,*

$C_6H_5NH-NHCS.OCH_3$ .—When methylethyl dithiocarbonate,  $CH_3OCS.SC_2H_5$ , was warmed with phenylhydrazine and then cooled, nothing but an oil was obtained. However, on treating this with ether and alkali, a solid separated which was identical with the above described thiolcarbazinimethyl ester melting at  $152^\circ$  (analysis C). On adding hydrochloric acid to the alkaline extract and crystallizing the precipitate from alcohol, yellow prisms were obtained melting about  $113^\circ$ . A nitrogen determination gave (analysis D):

	Calculated for $C_8H_{10}N_2OS$ .	C. Found.	D.
N	15.3	15.1	15.3

The ether extract contained the hydrazone,

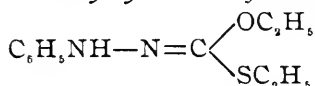
$C_6H_5NH-N=C \begin{array}{l} \nearrow OCH_3 \\ \searrow SC_2H_5 \end{array}$ , which decomposed when an attempt was made to purify it by distillation under reduced pressure.

*α-Benzoylphenylthioncarbazinicethyl Ester,*

.—When the thioncarbazinic ester is treated with benzoyl chloride, action begins about 90° and is complete on heating to 120° for a short time. On crystallizing from alcohol, fine colorless pyramids are obtained melting at 173°. This material is soluble in alkali in which solution it can be boiled without decomposition. A nitrogen determination gave :

	Calculated for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ .	Found.
N	9.3	9.3

The sodium salt of thioncarbazinicethyl ester was prepared by mixing the thion derivative with sodium alcoholate and evaporating in a vacuum. It forms a yellowish-red powder. When this was treated with benzoyl chloride the above benzoyl compound was obtained.

*Phenylhydrazone of Diethylthiocarbonic Ester,*

.—As stated above, under the heading of phenylthioncarbazinicethyl ester, from 115 grams of xanthogenic ester and the calculated quantity of phenylhydrazine, 37 grams of this hydrazone were obtained. In our first experiments with this substance, it was freed from the thion ester by shaking with alkali, and, after drying, it was distilled under reduced pressure. It was found that it invariably decomposed to some extent when treated in this way, although it boiled for the most part, at 190°–191° at 14 mm. pressure, and at 210°–213° at 36 mm. pressure. Thus obtained, it formed a thick yellowish-red oil which soon became dark-brown and resinous on exposure to the air. A nitrogen determination in a portion which had been distilled indicated that the substance obtained in this manner was not pure (analysis E).

It is better prepared from phenylthioncarbazinicethyl ester by treating the alcoholic solution with potash and ethyl iodide. Action takes place at ordinary temperature and, on filtering and evaporating, washing with water and drying over calcium

chloride, it was found to distil at  $198^{\circ}$  at 20 mm. pressure. A nitrogen determination gave (analysis F):

N	Calculated for $C_{11}H_{16}N_2OS.$	Found.	
	12.5	E.	F.
		11.5	12.9

The alcoholic solution gives with ferric chloride a garnet-red solution. When hydrogen sulphide was led into this oil at a temperature of  $125^{\circ}$  for two hours and the material then allowed to cool, a mass of needles or prisms separated. The material was soluble in alkali and, on precipitating with hydrochloric acid and crystallizing from alcohol, fine needles melting at  $73^{\circ}$  were obtained. This material was, therefore, phenylthioncarbazinicethyl ester.

When hydrogen chloride is led into the hydrazone, dissolved in ether or benzene, a colorless precipitate forms which rapidly deliquesces on exposure. On rapidly pressing it on paper, it was found to melt at about  $57^{\circ}$  giving off ethyl chloride and leaving a residue of phenylthiolcarbazinicethyl ester.

*Phenylhydrazone of Diethylthiocarbonic Ester and Thiobenzoic Acid.*—35 grams of the hydrazone were mixed with 20 grams of thiobenzoic acid and warmed on the steam-bath for twelve hours. On cooling, the material partially solidified. It was filtered as far as possible on the pump, and the solid material was crystallized from alcohol when prismatic crystals were obtained, melting constantly at  $112^{\circ}$ . These proved to be *phenylthiolcarbazinicethyl ester*. The oil filtered from this was distilled at 16 mm. pressure whereupon it boiled mostly at  $129^{\circ}$ – $131^{\circ}$ . It was redistilled several times at ordinary pressure (760 mm.), and although it decomposed slightly by this treatment, it boiled constantly at  $252^{\circ}$ – $253^{\circ}$ . The boiling point of *ethyl thiolbenzoate*,  $C_6H_5CO.SC_2H_5$  is given by Engelhardt, Latschinoff and Malyscheff<sup>1</sup> as  $243^{\circ}$  and by Seifert<sup>2</sup> as  $241^{\circ}$ – $243^{\circ}$ . In order to compare the above oil with ethyl thiolbenzoate, thiobenzoic acid, freshly prepared, was treated with alkali and ethyl bromide in alcohol, when action took place, on warming, and was complete in a few minutes.

<sup>1</sup> Ztschr. Chem., 1868, 356.

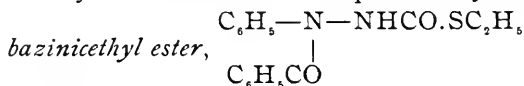
<sup>2</sup> J. prakt. Chem. (2), 31, 471.

Water was then added and the oil taken up in ether, dried and distilled, when it practically all boiled over from  $252^{\circ}$  to  $253^{\circ}$ . On mixing this oil with the above, the boiling-point of the mixture was unaltered. The material was therefore ethyl thiolbenzoate, and the previous observations on the boiling-point of this ester are  $10^{\circ}$  too low, our observations being taken with an Anschütz thermometer.

*Phenylhydrazone of Diethylthiocarbonic Ester and Benzoyl Chloride.*—5.7 grams of the hydrazone were mixed with 3.5 grams of benzoyl chloride in the cold, when the mixture became warm and effervesced, giving off ethyl chloride. On cooling, the material was crystallized from benzene and alcohol, when small lozenge-shaped crystals were obtained melting constantly at  $138^{\circ}$ – $139^{\circ}$ . It dissolves in alkali and is precipitated unaltered by acids and a nitrogen determination gave :

	Calculated for $C_{16}H_{16}N_2O_4S$ .	Found.
N	9.3	9.3

When this material is boiled with hydrochloric acid and alcohol it slowly decomposes and goes into solution. On adding sodium hydrate and crystallizing the precipitate thus produced, phenylthiolcarbazinicethyl ester melting at  $112^{\circ}$  is obtained. This same benzoyl derivative is formed when the thiolcarbazinic ester is warmed to  $100^{\circ}$  with benzoyl chloride. When it is heated with aniline, it gives carbanilide. This benzoyl derivative is in all probability  $\alpha$ -benzoylphenylthiol-



When the above hydrazone is diluted with benzene and acetyl chloride is added, a violent effervescence takes place. The product obtained after evaporation consists of a varnish which slowly solidifies. Beyond showing that it is readily soluble in alcohol and benzene it was not further examined. The hydrazone reacts with methyl iodide in the cold and well crystallized prisms separate. These will be investigated later, it being our intention to examine other hydrazones of the carbonic esters along similar lines.

*Thioncarbanilicmethyl Ester*,  $C_6H_5NHCS.OCH_3$ .—30 grams

of phenyl mustard oil and 120 grams of methyl alcohol when boiled for 12 hours on the steam-bath, gave 29 grams of material melting at  $95^{\circ}$ – $96^{\circ}$ , after crystallizing from alcohol. This compound has recently been prepared by Orndorff and Richmond<sup>1</sup> and they give its melting-point at  $97^{\circ}$ . A nitrogen determination gave :

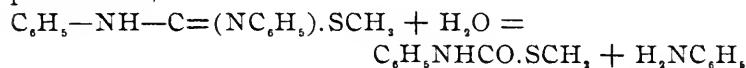
	Calculated for $C_6H_5NSO$ .	Found.
N	8.38	8.31

This substance gives a white precipitate with thallium hydrate which becomes black on boiling. When its alcohol solution was boiled with mercuric oxide, desulphurization took place slowly and, on concentrating the solution, carbanilide was obtained.

*Thiolcarbanilicmethyl Ester*,  $C_6H_5NHCO.SCH_3$ .—2 grams of the above compound were warmed with 2 grams of methyl iodide, and the product was crystallized from alcohol, when colorless plates were obtained melting at  $81^{\circ}$ – $83^{\circ}$ . This same compound was obtained when 5 grams of phenylthionethyl carbamate was heated on the steam-bath with 10 grams of methyl iodide. A nitrogen determination gave :

	Calculated for $C_6H_5NSO$	Found.
N	8.38	8.44

This material gives a reddish-yellow precipitate with thallium hydrate which does not blacken on boiling (difference from the thion compound). It gives white precipitates with lead and silver nitrates, and it dissolves in concentrated sulphuric acid, and is precipitated out by water. It agrees therefore in properties with the compound obtained by Will<sup>2</sup> from phenylimidophenylthiocarbamicmethyl ester and sulphuric acid,



*Thioncarbanilicethyl Ester*,  $C_6H_5NHCS.OC_2H_5$ , was prepared by boiling phenyl mustard oil with alcohol.<sup>3</sup> It was

<sup>1</sup> This Journal, 22, 462.

<sup>2</sup> Ber. d. chem. Ges., 15, 341.

<sup>3</sup> Hofmann: Ber. d. chem. Ges., 2, 120; 3, 772; Liebermann: Ann. Chem. (Liebig), 207, 142, Orndorff and Richmond: This Journal, 22, 461.

converted into *thiolcarbanilicethyl ester*,  $C_6H_5NHCO.SC_2H_5$ .—When 5 grams of thioncarbanilicethyl ester were heated for 12 hours with 15 grams of ethyl iodide on the steam-bath and the product crystallized from alcohol, a mass of colorless needles was obtained, melting from  $71^\circ$  to  $73^\circ$ . This compound has already been prepared by Will by a different method.<sup>1</sup> When boiled with a mixture of alcohol and concentrated ammonia it gave monophenylurea melting at  $147^\circ$ . Although this compound differs from the thion derivative by about  $1^\circ$  in melting-point, when portions of each are mixed, the melting-point is lowered about  $35^\circ$ .

*Thioncarbanilicisobutyl Ester*,  $C_6H_5NH-CS.OC_4H_9$ .—Orndorff and Richmond state that heating isobutyl alcohol and phenyl mustard oil in sealed tubes at temperatures varying from  $110^\circ$  to  $180^\circ$  gave no solid product except thiocarbanilide. They prepared this substance by heating the materials for twenty hours on the water-bath, and state that it melts at  $80.5^\circ$ .

We found that, when 10 grams of phenyl mustard oil and 20 grams of isobutyl alcohol were heated in a closed tube for  $115^\circ$  to  $125^\circ$  for three hours, beautiful, long, colorless prisms were obtained which, after crystallization from alcohol, melted at  $77^\circ$ – $78^\circ$ . A nitrogen determination gave :

	Calculated for $C_{11}H_{15}NSO$ .	Found.
N	6.69	6.76

When 2.5 grams of the above compound were heated with 2.3 grams of isobutyl iodide in an oil-bath from  $125^\circ$  to  $140^\circ$  no action whatever was observed.

*Ethyl Thioncarbamate*,  $H_2NCSOC_2H_5$ , and *Chloroacetic Acid* were mixed in molecular proportions and heated on the steam-bath until ethyl chloride ceased being evolved. The mass was then pressed on a plate, taken up in ether and filtered. The ether was then evaporated and the residue extracted with benzene. On crystallizing the material from water and ether, it melted at  $135^\circ$ – $136^\circ$  with effervescence. A nitrogen determination gave :

	Calculated for $H_2NCO.SCH_2COOH$ .	Found.
N	10.37	10.20

<sup>1</sup> Loc. cit.



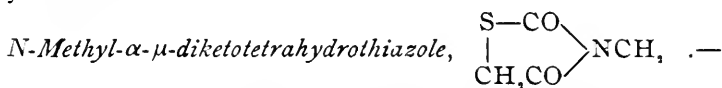
This material is therefore carbaminthioglycollic acid,  $\text{H}_2\text{NCO.SCH}_2\text{COOH}$ . The yield was poor, as thioglycollic acid, thioethyl carbamate and cyanuric acid were also formed.

*Isoamyl Thioncarbamate*,  $\text{H}_2\text{NCSOC}_3\text{H}_{11}$ , and *Chloracetic Acid*, when heated on the steam-bath, deposited crystals which when crystallized from ether separated in the form of six-sided prisms melting at  $123^\circ\text{--}125^\circ$ . A nitrogen determination gave:

	Calculated for $\text{C}_2\text{H}_5\text{NSO}_2$	Found.
N	11.96	11.65

This material is therefore the so-called mustard oil acetic acid, or  $\alpha$ - $\mu$ -diketotetrahydrothiazole. This compound is formed far more readily by boiling the sulphocyanacetic esters with concentrated hydrochloric acid. It can be boiled under diminished pressure without decomposition. At 19 mm. pressure it boiled from  $178.5^\circ$  to  $179.5^\circ$ .

*Silver  $\alpha$ - $\mu$ -diketotetrahydrothiazole* was prepared by precipitating the alkaline solution of the above compound with the calculated quantity of silver nitrate. It forms a light yellow powder which turns brown in the sunlight. A silver determination gave 49.8 per cent silver instead of 48.2 per cent. Hydrogen sulphide regenerates the thiazole from this salt. The same result was obtained when it was treated with benzoyl chloride.



The above silver salt when suspended in ether and in benzene and heated for several days with methyl iodide, gave a product which boiled at 15 mm. pressure from  $131^\circ$  to  $132^\circ$ . This distillate solidified at once, on cooling, and when crystallized from benzene and ligroin, melted from  $37^\circ$  to  $39^\circ$ . A nitrogen determination gave:

	Calculated for $\text{C}_4\text{H}_5\text{NSO}_2$	Found.
N	10.6	10.5

For purposes of comparison  $\alpha$ - $\mu$ -diketotetrahydrothiazole was methylated according to the method employed by

Arapides<sup>1</sup>, when a product was obtained which boiled at 14 mm. pressure from 129° to 131° and was otherwise identical with the product from the silver salt. Arapides has shown that this product has the methyl group attached to nitrogen. He states that it forms an oil which slowly solidifies over sulphuric acid and that it very readily deliquesces. This is not the case when the material is purified by distillation; it then readily solidifies and does not deliquesce on exposure.

When 1.4 gram of N-methyl- $\alpha$ - $\mu$ -diketotetrahydrothiazole, prepared either from the sodium or silver salt, was treated with 4.2 grams of sodium hydrate and 1.8 grams of silver nitrate added in aqueous solution, a gas was given off and a white gelatinous precipitate was obtained which turned yellow in the light. The gas was found to be carbon dioxide, and a silver determination in the precipitate gave 70.2 per cent, while the calculated percentage for silver thioglycollate  $\text{AgSCH}_2\text{COOAg}$ , is 70.5 per cent.

When this salt was decomposed with hydrogen sulphide, in aqueous solution, the filtrate gave with ferric chloride and ammonia the characteristic red-violet color of thioglycollic acid.

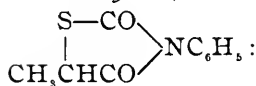
*Thioncarbanilicethyl Ester*,  $\text{C}_6\text{H}_5\text{NHCSOC}_2\text{H}_5$ , and *Chloracetic Acid* react on the steam-bath giving off ethyl chloride and water, and not hydrochloric acid and alcohol. The product when crystallized from alcohol forms long colorless needles and melts from 147° to 148°, which is the melting-point of *n*-phenyl- $\alpha$ - $\mu$ -diketotetrahydrothiazole (Phenylsenfölglycolid), as found by Liebermann.<sup>2</sup> This reaction is much smoother than in the case of ethyl thioncarbamate and chloracetic acid.

*Thioncarbanilicethyl Ester and  $\alpha$ -Brompropionicethyl Ester* (by G. K. Dustin).—When 13 grams of brompropionicethyl ester were heated with one molecular proportion of thioncarbanilicethyl ester for some time on the water-bath, then for a number of hours from 120°–140°, a solid separated, on cooling. This crystallized from alcohol in groups of fine, colorless needles melting at 103° and a nitrogen determination agreed with the calculated for

<sup>1</sup> Ann. Chem. (Liebig), **249**, 28.

<sup>2</sup> Loc. cit.

*n*-Phenyl- $\alpha$ - $\mu$ -diketo- $\beta$ -methyltetrahydrothiazole,



N	Calculated for	Found.	
	$\text{C}_{10}\text{H}_9\text{NO}_2\text{S}$ .	I.	II.
	6.7	6.7	6.6

*Thioncarbanilicethyl Ester and  $\alpha$ -Bromisobutyricethyl Ester*, when heated for ten hours from  $130^\circ$ – $155^\circ$ , gave a solid, which, when crystallized from dilute alcohol, separated in the form of colorless prisms or pyramids and melted at  $79^\circ$ – $81^\circ$ . A nitrogen determination shows that this compound is *carbanil- $\alpha$ -thioisobutyricethyl ester*,  $\text{C}_6\text{H}_5\text{NHCO}.\text{SC}(\text{CH}_3)_2\text{CO}_2\text{C}_2\text{H}_5$ :

N-	Calculated for	Found.
	$\text{C}_{13}\text{H}_{17}\text{SNO}_2$ .	
	5.2	4.9

This compound can be boiled with concentrated hydrochloric acid and recovered unaltered. When  $\alpha$ -bromisobutyric acid and thioncarbanilicmethyl ester were heated as above, the only solid material isolated was aniline hydrobromide. This crystallized in plates which darkened at  $245^\circ$  and became black and melted with effervescence at about  $280^\circ$ . A bromine determination gave 46.2 per cent; calculated 45.9 per cent.

The following sulphocyan derivatives of the fatty esters  $\text{NCS}-\text{CHRCO}_2\text{R}'$ , are obtained in good yields by boiling the corresponding alpha-halogen esters with potassium sulphocyanide in alcoholic solution. They are oils with a penetrating, persistent, and, for the most part, disagreeable odor. They can be distilled unaltered under reduced pressure.

The boiling-points which are given in the following experiments represent the temperatures at which the greater portion of the esters were collected. For the preparation of the sulphocyanides, in some cases, the bromesters were collected under wider limits than those given in the tables, the bromesters being freshly prepared from Kahlbaum's acids by the Hell-Volhard-Zelinsky method.

*Experiments by Leeds Mitchell.*

*Methyl Sulphocyanacetate*,  $\text{NCS}.\text{CH}_2\text{CO}_2\text{CH}_3$ .—75 grams

of methyl chloracetate, 80 grams of absolute alcohol, and 60 grams of potassium sulphocyanide, after boiling twenty-four hours, gave 38 grams of methyl sulphocyanacetate, boiling from  $120^{\circ}$ – $122^{\circ}$  at 16 mm. pressure.

*Ethyl Sulphocyanacetate* boiled at  $118^{\circ}$ – $122^{\circ}$  at 15 mm. pressure. Heintz,<sup>1</sup> who first prepared this ester, states that it boils in a vacuum at  $118^{\circ}$ – $200^{\circ}$ , and Claesson found that it boils with partial decomposition at  $225^{\circ}$  at ordinary pressure.

*Isoamyl Sulphocyanacetate* boiled at  $145^{\circ}$ – $147^{\circ}$  at 17 mm. pressure, while Claesson found that it boils at  $255^{\circ}$  at ordinary pressure.

*$\alpha$ - $\mu$ -Diketotetrahydrothiazole* (*mustard-oil acetic acid*, *Senf-ölessigsäure*),  $\begin{array}{c} \text{CH}_2\text{CO} \\ | \\ \text{S}-\text{CO} \end{array} \rangle \text{NH}$ .--38 grams of methyl sul-

phocyanacetate and 76 grams of concentrated hydrochloric acid were boiled a few minutes until all the oil dissolved. The solution was then evaporated and the residue treated with benzene and filtered from ammonium chloride. The material dissolved by benzene was crystallized from water until it melted at  $125^{\circ}$ – $126^{\circ}$ . In this manner 2 grams of ammonium chloride and 20 grams of  $\alpha$ - $\mu$ -diketotetrahydrothiazole were obtained. This product is identical in every respect with that obtained by heating isoamyl thioncarbamate with chloracetic acid as described above.

#### *Experiments by Guy K. Dustin.*

*Methyl  $\alpha$ -Sulphocyanpropionate*,  $\text{CH}_3\text{—CH}.\text{SCN}.\text{CO}_2\text{CH}_3$ .—This was prepared by boiling 57 grams of methyl  $\alpha$ -bromopropionate with one molecular proportion of potassium sulphocyanide and twice its weight of alcohol until a test with ferric chloride showed no potassium sulphocyanide. This required ten hours. After filtering and evaporating the alcohol, practically the entire product boiled from  $104^{\circ}$ – $106^{\circ}$  at 15–16 mm. pressure. The yield obtained was 34 grams, while the calculated yield is 46 grams.

Nitrogen determinations gave the following results :

<sup>1</sup> *Loc. cit.*

	Calculated for $C_6H_7NSO_2$ .	I.	Found.	II.
N	9.65	10.1		10.2

The material was obtained as a colorless oil with a strong, peculiar, but not unpleasant, odor.

*Ethyl  $\alpha$ -Sulphocyanpropionate.*—When 30 grams of ethyl  $\alpha$ -bromopropionate were boiled with one molecular proportion of potassium sulphocyanide, it required two days before the action was complete. On distilling the reaction-product at 16 mm. pressure it all boiled at  $104^{\circ}$ – $110^{\circ}$ , mostly at  $107^{\circ}$ – $108^{\circ}$ . The yield was 22 grams and an analysis of the colorless oil thus obtained gave :

	Calculated for $C_6H_9NSO_2$ .	Found.
N	8.8	8.9

*Isobutyl  $\alpha$ -Sulphocyanpropionate* was obtained when 71 grams of isobutyl  $\alpha$ -bromopropionate was boiled in alcoholic solution with 33 grams of potassium sulphocyanide. On distilling at 15 mm. pressure, 38 grams of clear, colorless oil, boiling at  $130^{\circ}$ – $131^{\circ}$  were collected, the odor of which was not unpleasant. A nitrogen determination gave :

	Calculated for $C_6H_{13}NSO_2$ .	Found.
N	7.48	7.48

*Isoamyl  $\alpha$ -Sulphocyanpropionate* was prepared by boiling 87 grams of the brom ester with potassium sulphocyanide and alcohol for seven hours. It boiled at  $141^{\circ}.5$  at 15 mm. pressure, and the yield was 67 grams. It was thus obtained as a colorless oil, the odor of which was not unpleasant. A nitrogen determination gave :

	Calculated for $C_8H_{15}NSO_2$ .	Found.
N	6.9	7.0

When this oil is distilled at ordinary pressure it boils with decomposition at  $265^{\circ}$ – $267^{\circ}$ .

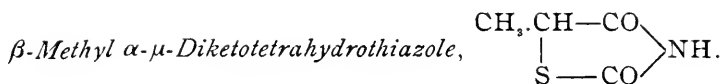
The boiling-points of the  $\alpha$ -bromopropionic esters used in making the above sulphocyan derivatives were as follows :

The *methyl ester* boiled at  $51^{\circ}.5$  at 19 mm. pressure.

The *ethyl ester* boiled at  $56^{\circ}$ – $58^{\circ}$  at 14 mm. pressure.

The *isobutyl ester* boiled at  $79^{\circ}$ – $80^{\circ}$  at 14 mm. pressure.

The *isoamyl ester* boiled at  $99^{\circ}$ – $100^{\circ}$  at 16 mm. pressure.



—The best yield of this substance was obtained from the methyl ester. 11 grams of methyl  $\alpha$ -sulphocyanpropionate and 15 grams of concentrated hydrochloric acid were mixed and evaporated to dryness on the steam-bath. Benzene then removed 0.6 gram of ammonium chloride, and 7.8 grams of crude thiazole were obtained. This, when crystallized from a mixture of benzene and ligroin, separated in the form of colorless leaves and melted from  $46^\circ$ – $47^\circ$ , and nitrogen determinations gave the following :

	Calculated for $\text{C}_4\text{H}_5\text{NSO}_2$ .	I.	Found.	II.
N	10.6	10.5		10.5

On distilling it at 20 mm. pressure it boiled, for the most part, from  $165^\circ$ – $168^\circ$ . Silver nitrate added to the alkaline solution of this substance produces a bulky, white, but not gelatinous, precipitate of the silver salt. It is decomposed by warm water.

*Experiments by Harry LeB. Gray.*

*Methyl α-Sulphocyanisobutyrate*,  $(\text{CH}_3)_2\text{C.SCN.CO}_2\text{CH}_3$ , was obtained in a similar manner to the preceding sulphocyanides as a heavy, colorless oil having a disagreeable, penetrating odor. It boiled for the most part from  $101^\circ$ – $102^\circ$  at 17 mm. pressure. This fraction was analyzed with the following result :

	Calculated for $\text{C}_6\text{H}_9\text{NSO}_2$ .	Found.
N	8.8	8.9

*Ethyl α-Sulphocyanisobutyrate* resembles the methyl ester in properties. The greater portion boiled at  $111^\circ$ – $115^\circ$  at 22 mm. pressure. A nitrogen determination gave :

	Calculated for $\text{C}_7\text{H}_{11}\text{NSO}_2$ .	Found.
N	8.09	8.68

*Isobutyl α-Sulphocyanisobutyrate*.—The product in this case, after several distillations, boiled at  $132^\circ$ – $133^\circ$  at 21 mm. pressure. This fraction gave the following result on analysis :

	Calculated for $C_9H_{15}NSO_2$ .	Found.
N	6.96	6.90

*Isoamyl α-Sulphocyanisobutyrate*, on fractioning, boiled at  $135^{\circ}.5$ – $136^{\circ}.5$  at 16 mm. pressure. A nitrogen determination gave :

	Calculated for $C_{10}H_{17}NSO_2$ .	Found.
N	6.5	7.1

This material, like the preceding, is a colorless oil with a penetrating, disagreeable odor.

The boiling-points of the  $\alpha$ -bromisobutyric esters used in making the above sulphocyan derivatives were as follows :

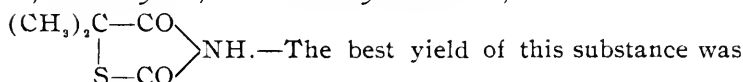
The *methyl ester* boiled at  $51^{\circ}$ – $52^{\circ}$  at 19 mm. pressure.

The *ethyl ester* boiled at  $70^{\circ}$ – $71^{\circ}$  at 20 mm. pressure.

The *isobutyl ester* boiled at  $83^{\circ}$ – $85^{\circ}$  at 16 mm. pressure.

The *isoamyl ester* boiled at  $107^{\circ}$ – $108^{\circ}$  at 25 mm. pressure.

$\beta$ -Dimethyl  $\alpha$ - $\mu$ -Diketotetrahydrothiazole,



obtained from the methyl ester ; the amyl ester failed to give the compound. Fourteen grams of methyl  $\alpha$ -sulphocyanisobutyrate were mixed with 20 cc. concentrated hydrochloric acid and heated on the steam-bath for about one hour. The reaction is complete when no more oil remains on the surface of the liquid. The solution, when evaporated, gave 1 gram of ammonium chloride, the remaining material being the thiazole derivative. This crystallizes from water in enormously lengthened, colored prisms, one crystal being obtained that measured 31 mm. long and 1.5 mm. in diameter. It melts at  $79^{\circ}$ – $80^{\circ}$ , and a nitrogen determination gave :

	Calculated for $C_6H_7NSO_2$ .	Found.
N	9.65	9.87

#### Experiments by Henry A. North.

*Methyl α-Sulphocyanbutyrate*,  $C_4H_7CH_2SCN.CO_2CH_3$ .—This was obtained as a colorless oil boiling at  $125^{\circ}$  at 23 mm. pressure, and a nitrogen determination gave the following result :

	Calculated for $C_6H_9NSO_2$ .	Found.
N	8.8	8.6

*Ethyl  $\alpha$ -Sulphocyanbutyrate*.—On mixing 100 grams of the bromester, 49.6 grams of potassium sulphocyanide, and 200 cc. of alcohol, and boiling for twelve hours, somewhat more than 65 grams of a clear, colorless oil was obtained. This boiled from  $134^\circ$ – $136^\circ$  at 28 mm. pressure. Like the other members of this series, it has a strong, unpleasant, extremely persistent odor. A nitrogen determination gave the following result :

	Calculated for $C_6H_{11}NSO_2$ .	Found.
N	8.09	8.35

*Isoamyl  $\alpha$ -Sulphocyanbutyrate* was obtained as a colorless oil which, after fractionation boiled from  $158^\circ$  to  $160^\circ$  at 23 mm. pressure. A nitrogen determination gave :

	Calculated for $C_{10}H_{17}NSO_2$ .	Found.
N	6.51	6.37

The boiling-points of the  $\alpha$ -brom normal butyric esters used in making the above sulphocyan derivatives were as follows :

The *methyl ester* boiled at  $67^\circ$ – $72^\circ$  at 25 mm. pressure.

The *ethyl ester* boiled at  $68^\circ$ – $69^\circ$  at 19 mm. pressure.

The *isoamyl ester* boiled at  $110.5^\circ$ – $113.5^\circ$  at 19 mm. pressure.

*$\beta$ -Ethyl  $\alpha$ - $\mu$ -Diketotetrahydrothiazole*,  $C_2H_5CH-CO \begin{array}{c} | \\ S - CO \end{array} \rangle NH$ .—

This is best obtained from the methyl or ethyl esters. On warming these with concentrated hydrochloric acid, until solution took place and then evaporating, a colorless oil was obtained which solidified on cooling. When crystallized from a mixture of benzene and ligroin, six-sided prisms separated which finally melted from  $63^\circ$  to  $65^\circ$ , and a nitrogen determination gave the following result :

	Calculated for $C_5H_7NSO_2$ .	Found.
N	9.65	9.68



*Experiments by W. H. Buell.**Methyl  $\alpha$ -Sulphocyanisovalerianate,*

$(\text{CH}_3)_2\text{CH}-\text{CH}.\text{SCN}.\text{CO}_2\text{CH}_3$ .—39 grams of the brom ester, 78 grams of alcohol and 19.4 grams of potassium sulphocyanide, warmed on the water-bath for two days, gave 14 grams of colorless oil boiling from  $119^\circ$  to  $121.5^\circ$  at 23 mm. pressure. It has a peculiar penetrating unpleasant odor. A nitrogen determination gave :

	Calculated for $\text{C}_7\text{H}_{11}\text{NSO}_2$ .	Found.
N	8.09	8.35

*Ethyl  $\alpha$ -Sulphocyanisovalerianate.*—88 grams of the brom ester, 40.8 grams of potassium sulphocyanide and 176 grams of alcohol were boiled for three days. On fractioning, 34 grams of ester were obtained, boiling from  $126^\circ$  to  $128^\circ$  at 19 mm. pressure. This was analyzed with the following result :

	Calculated for $\text{C}_8\text{H}_{13}\text{NSO}_2$ .	Found.
N	7.48	7.85

*Isobutyl  $\alpha$ -Sulphocyanisovalerianate.*—55 grams of the brom ester, 22.5 grams of potassium sulphocyanide and 110 grams of alcohol gave 19 grams of oil, boiling, for the most part, from  $145^\circ$  to  $147^\circ$  at 19 mm. pressure. This gave the following result on analysis :

	Calculated for $\text{C}_{10}\text{H}_{17}\text{NSO}_2$ .	Found.
N	6.5	5.8

This ester, like the above, had a strong, peculiar odor which, perhaps, was not unpleasant.

*Isoamyl  $\alpha$ -Sulphocyanisovalerianate.*—105 grams of the brom ester, 210 grams of alcohol and 40.6 grams of potassium sulphocyanide gave a colorless oil with a disagreeable odor after boiling for two days. The greater portion of this boiled from  $151^\circ$  to  $152^\circ$  at 14 mm. pressure and a nitrogen determination gave the following result :

	Calculated for $\text{C}_{11}\text{H}_{19}\text{NSO}_2$ .	Found.
N	6.11	6.32

The boiling-points of the  $\alpha$ -bromisovalerianic esters used in making the above sulphocyan derivatives were as follows :

The *methyl ester* boiled from  $174^{\circ}$ – $182^{\circ}$  at 760 mm. pressure.

The *ethyl ester* boiled from  $186^{\circ}$ – $187^{\circ}$  at 764 mm. pressure.

The *isobutyl ester* boiled from  $105^{\circ}$ – $108^{\circ}$  at 17 mm. pressure.

The *isoamyl ester* boiled from  $113^{\circ}$ – $114^{\circ}$  at 16 mm. pressure.

When the above sulphocyanic esters were boiled with hydrochloric acid the products were oils in each case. The ethyl ester gave a product which solidified in a freezing-mixture, but, on attempting to crystallize it, or on removing it from the freezing-mixture, it became liquid, and, on attempting to distil it under diminished pressure, it decomposed.

For convenience of reference, the boiling-points of the sulphocyanic esters, described by us, are collected in the following table :

	Pressure in mm.	Boiling-point.
<i>Methyl <math>\alpha</math>-Sulphocyanacetate</i>	16	$120^{\circ}$ – $122^{\circ}$
<i>Ethyl</i> “	15	$118^{\circ}$ – $122^{\circ}$
<i>Isoamyl</i> “	17	$145^{\circ}$ – $147^{\circ}$
<i>Methyl <math>\alpha</math>-Sulphocyanpropionate</i>	15–16	$104^{\circ}$ – $106^{\circ}$
<i>Ethyl</i> “	16	$107^{\circ}$ – $108^{\circ}$
<i>Isobutyl</i> “	15	$130^{\circ}$ – $131^{\circ}$
<i>Isoamyl</i> “	15	$141.5^{\circ}$
<i>Methyl <math>\alpha</math>-Sulphocyanisobutyrate</i>	17	$101^{\circ}$ – $102^{\circ}$
<i>Ethyl</i> “	22	$111^{\circ}$ – $115^{\circ}$
<i>Isobutyl</i> “	21	$132^{\circ}$ – $133^{\circ}$
<i>Isoamyl</i> “	16	$135.5^{\circ}$ – $136.5^{\circ}$
<i>Methyl <math>\alpha</math>-Sulphocyanbutyrate</i>	23	$125^{\circ}$
<i>Ethyl</i> “	28	$134^{\circ}$ – $136^{\circ}$
<i>Isoamyl</i> “	23	$158^{\circ}$ – $160^{\circ}$
<i>Methyl <math>\alpha</math>-Sulphocyanisovalerianate</i>	23	$119^{\circ}$ – $121.5^{\circ}$
<i>Ethyl</i> “	19	$126^{\circ}$ – $128^{\circ}$
<i>Isobutyl</i> “	19	$145^{\circ}$ – $147^{\circ}$
<i>Isoamyl</i> “	14	$151^{\circ}$ – $152^{\circ}$

# THE CONDUCTIVITY TEMPERATURE COEFFICIENT OF SOME LIQUID AMMONIA SOLUTIONS.

BY EDWARD C. FRANKLIN AND CHARLES A. KRAUS.

It was first established by Kohlrausch<sup>1</sup> that the electrical conductivity of aqueous solutions of electrolytes increases with the temperature, and that for ordinary temperatures this relation may be represented by the linear function,

$$\lambda_t = \lambda_0 (1 + bt).$$

Arrhenius,<sup>2</sup> however, from theoretical considerations, has shown that the relation between temperature and conductivity is not a linear one, but that the conductivity at first increases with the temperature, reaches a maximum value, and then decreases. He deduced an exponential equation to represent the relation between temperature and conductivity and found by experiment that in the case of hypophosphorous acid and phosphoric acid his calculated maximum temperatures agree with his observations. He calculated the maxima for a number of salts, acids, and bases, but the temperatures of maximum molecular conductivity generally lie too high for experimental verification.

Further investigations upon the effect of changes of temperature on the conductivity of aqueous solutions have been made by Trötsch,<sup>3</sup> Krannhals,<sup>4</sup> Sack,<sup>5</sup> Schroeder,<sup>6</sup> Rudolphi,<sup>7</sup> Euler,<sup>8</sup> Bauer,<sup>9</sup> and Schaller.<sup>10</sup>

Since the measurements of Arrhenius on phosphoric acid and hypophosphorous acid, maxima of conductivity have been established for solutions of copper sulphate and of a number of organic acids, while according to the investigations of Cattaneo<sup>11</sup> all ethereal solutions of electrolytes and alcoholic

<sup>1</sup> Pogg. Ann., **154**, 228 (1875).

<sup>2</sup> Ztschr. phys. Chem., **4**, 96 (1889).

<sup>3</sup> Wied. Ann., **41**, 256 (1890).

<sup>4</sup> Ztschr. phys. Chem., **5**, 250 (1890).

<sup>5</sup> Wied. Ann., **43**, 212 (1891).

<sup>6</sup> Ztschr. phys. Chem., **16**, 72 (1895).

<sup>7</sup> *Ibid.*, **17**, 377 (1895).

<sup>8</sup> *Ibid.*, **21**, 257 (1896).

<sup>9</sup> *Ibid.*, **23**, 409 (1897).

<sup>10</sup> *Ibid.*, **25**, 497 (1898).

<sup>11</sup> Beibl. Wied. Ann., **18**, 219, 365 and 1085 (1894).

solutions of the bromides and iodides exhibit negative temperature coefficients.

Most of the measurements made by the investigators mentioned above are confined to temperatures below  $52^{\circ}$ , some of them reach  $100^{\circ}$ , while only those of Sack on copper sulphate exceed this temperature. Sack followed the conductivity of copper sulphate solution to  $124^{\circ}$  when his conductivity cell exploded. A very serious obstacle to carrying such measurements to higher temperatures is the solvent action of the water on the glass resistance vessel, which even at  $100^{\circ}$  becomes so great as seriously to interfere with the accuracy of the measurements. Certainly at temperatures from  $100^{\circ}$  to  $200^{\circ}$  or more above the boiling-point of water, temperatures which must be reached if the maxima predicted by Arrhenius are to be realized, the action of the solvent on the resistance cell would be so great as to prohibit even approximate measurements of conductivity. Furthermore, the very high tension of aqueous vapor at elevated temperatures, and especially at temperatures approaching the critical point, must render difficult the adaption of conductivity vessels for the purpose.

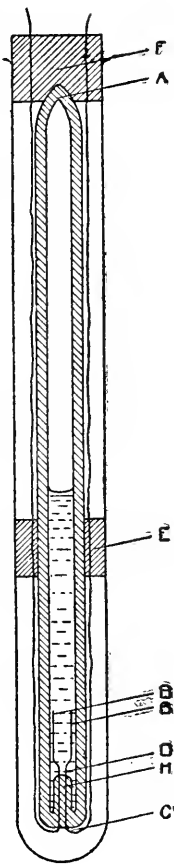
In ammonia, however, we have found an electrolytic solvent which lends itself much better to measurements of the conductivity of its solutions at temperatures far above its boiling-point at atmospheric pressure. The fact that it does not dissolve the materials of the glass vessels used eliminates at once a very serious obstacle in the way of such measurement, when water is used as the solvent. The temperatures of maximum conductivity lie below the ordinary temperature, which has enabled us to follow easily the negative branch of the curve for a considerable distance beyond the maximum, and even beyond the critical temperature of the solvent; conditions which would probably be difficult to control in the case of water.

#### *The Conductivity Vessel.*

Conductivity cells of the form indicated in the adjoining figure were devised and used in making the measurements recorded in this paper. The cell *A* is made of heavy-walled

glass tubing. *BB* are the electrodes, each of about 1 sq. cm. area. The leading-in wires, *C*, are of very fine platinum wire for the reason that tubes with larger wire invariably burst at high temperatures, especially as the pressure approached the critical pressure of the ammonia. At *D* sufficiently heavy wire was used to retain the electrodes in position. *E* and *F* are corks for holding the tube *A* in position within the outer thin-walled tube, which latter served the purpose of protecting the leading-in wires from injury. The conductivity tube thus protected was suspended in the temperature bath by means of the heavier copper connecting wires.

After platinizing the electrodes the resistance capacity of the cell was measured by means of a fiftieth-normal solution of potassium chloride. The tube was then cleaned, dried, and weighed. A weighed quantity of the solute was then placed in the tube and the air displaced by a slow current of ammonia gas from the stock cylinder. While maintaining the current of gas the tube was placed in a bath of liquid ammonia contained in a vacuum-jacketed test-tube, and liquid ammonia was drawn from the stock cylinder in the manner described in a previous paper,<sup>1</sup> until the liquid occupied from about one-third to one-half of the volume of the conductivity tube. The tube was then sealed off before the blow-pipe. The portion of the tube drawn off in sealing was preserved and weighed together with the sealed tube and its contents. The weight of ammonia contained in the tube was found by subtracting from the weight thus obtained, the weight of the empty tube plus the weight of the solute. It was not attempted in these preliminary experiments to determine the volume of the solution at the different temperatures. The



<sup>1</sup> This JOURNAL, 20, 839 (1898).

volume used in calculating the results given below was obtained by dividing the weight of ammonia contained in the tube by its specific gravity at its boiling-point ; viz., 0.68.<sup>1</sup>

*Method of Making the Determinations.*

The bridge and telephone method of Kohlrausch was used for measuring the resistances. For measurements at low temperatures the conductivity tube was immersed in a bath of carbon dioxide and ether contained in a vacuum-jacketed tube. The bath was allowed to warm up slowly and the temperatures were read at intervals of from 2°-10° by means of an air thermometer. For the higher temperatures a paraffin bath and a mercury thermometer were used.

The following results have been obtained :

*Ammonium Iodide.*

Weight of solute, 0.00830 gram.

“ “ solvent, 1.967 grams.

Cell constant, 0.1514.

Dilution,  $v$ , 50.76.

T.	$\mu_t$	T.	$\mu_t$
235	162.9	302	223.1
242	170.8	305	225.9
248	177.7	308	227.3
253	186.8	312	224.9
261	194.5	318	224.2
268	204.2	326	215.2
275	211.5	335	207.7
281	216.1	344	197.1
285	219.6	353	181.4
291	221.5	364	158.9
299	223.1		

*Ammonium Bromide.*

Weight of solute, 0.01365 gram.

“ “ solvent, 1.4965 grams.

Cell constant, 0.1571.

Dilution,  $v$ , 15.79.

<sup>1</sup> Lange : Ztschr. gesamt. Kält-Indust., 5, 1 (1898).

T.	$\mu_t$	T.	$\mu_t$
241	103.8	364	60.8
250	106.5	373	55.1
261	110.2	383	44.9
274	112.9	390	38.2
283	113.7	395	26.5
294	110.6	367	47.6
298	109.0	373	41.9
308	106.0	383	30.4
318	101.8	390	22.7
327	95.8	395	17.7
336	86.1	401	7.96
344	83.0	405	4.97
354	72.3	406	2.93

*Ammonium Chloride.*

Weight of solute, 0.01157 gram.

“ “ solvent, 2.122 grams.

Cell constant, 0.1548.

Dilution,  $v$ , 14.43.

T.	$\mu_t$	T.	$\mu_t$
235	70.9	277	77.5
245	73.0	279	76.9
248	73.9	285	76.0
253	74.5	290	75.3
257	75.1	292	73.9
262	76.0	295	72.1
267	76.6	298	68.8
273	76.6		

*Potassium Iodide.*

Weight of solute, 0.00121 gram.

Volume of solvent, 2.5 cc., approximate.

Cell constant, 0.1533.

Dilution,  $v$ , 34.30.

T.	$\mu_t$	T.	$\mu_t$
205	104.9	298	196.8
210	119.0	303	194.3
220	128.0	307	192.8
230	143.7	314	187.5
240	159.1	324	174.0
251	175.4	335	160.6
261	185.6	347	156.3

T.	$\mu_t$ .	T.	$\mu_t$ .
271	193.2	355	128.9
281	196.7	360	120.4
283	199.1	364	112.1
288	199.8	370	101.0
294	198.4	373	82.6

*Paranitrophenol.*

Weight of solute, 0.00571 gram.

" " solvent, 1.868 grams.

Cell constant, 0.1956.

Dilution,  $v$ , 67.07.

T.	$\mu_t$ .	T.	$\mu_t$ .
252	160.2	312	194.7
259	166.1	316	189.0
267	174.2	323	184.6
276	182.8	333	174.4
290	192.2	343	154.1
298	192.6	354	134.0
303	194.4	363	109.7

*Copper Nitrate.*

Weight of solute, 0.01068 gram.

" " solvent, 1.108 grams.

Cell constant, 0.2343.

Dilution,  $v$ , 28.51.

T.	$\mu_t$ .	T.	$\mu_t$ .
211	72.2	284	106.3
214	73.9	287	105.5
216	75.2	292	104.6
221	79.7	298	103.2
229	85.2	306	103.4
237	91.9	315	98.2
246	96.6	323	91.4
255	102.7	332	88.0
261	105.5	343	81.9
271	106.3	352	74.0
277	106.8	359	70.0

As this solution was heated up to higher temperatures there was deposited on the walls of the tube a slightly colored solid, which, as the critical temperature was approached, melted and flowed to the bottom of the tube as a blue liquid, leaving



the solution colorless. On cooling, the liquid diffuses through the solution, the latter thus regaining its original blue color. The conductivity of the solution after cooling was found to have increased considerably, due probably to chemical action between the solvent and solute. At  $140^{\circ}$ ,  $7^{\circ}$  above the temperature at which the meniscus had disappeared, the solution remained distinctly a conductor.

*Sulphur.*

Sulphur dissolves in ammonia to form a colored solution which is a fair conductor of electricity. What the substance is which is formed and acts as an electrolyte has not yet been investigated. As the solution was heated the conductivity increased until the temperature of  $60^{\circ}$  was reached. On repeating the experiment with the same tube later the conductivity of the solution was found to be much higher and the maximum was this time located at  $17^{\circ}$  instead of at  $60^{\circ}$ , as in the first experiment. This change of conductivity probably indicates chemical action between the solute and solvent. At temperatures above the maximum the conductivity decreased with increasing temperature reaching a value of 1.04 at  $139^{\circ}$ ,  $6^{\circ}$  above the critical temperature of ammonia.

Weight of solute, 0.00280 gram.

" " ammonia, 1.987 grams.

Cell constant, 0.1296.

Dilution,  $v$ , 53.5.

T.	$\mu_t$ .	T.	$\mu_t$ .
238	74.6	348	61.3
248	80.9	359	51.3
255	83.5	373	36.8
264	86.0	381	31.5
273	87.7	389	21.7
283	88.8	393	17.0
292	88.8	400	9.14
298	88.2	404	4.44
301	86.5	407	1.79
312	83.6	411	1.11
324	78.2	412	1.04
334	72.0		

In order to determine definitely whether or not the solution retains its power as a conductor above its critical temperature

and after the complete disappearance of the meniscus, the conductivity tube was slowly warmed up from  $121^{\circ}$  to  $139^{\circ}.5$ . The temperature rose very gradually during seven hours, which was the time used in making the series of measurements. At  $139^{\circ}.5$ ,  $6^{\circ}.5$  above the critical temperature, the solution still showed a distinct conductivity; *viz.*, 0.65 Kohlrausch unit.

	T.	$\mu_t$
I P.M.	394	13.6
	400	7.71
	403.7	3.79
	406	1.58 (1)
	409.1	0.95 (2)
	410	0.82 (3)
8 P.M.	412.5	0.65

(1) The meniscus gradually faded until it was impossible to detect the slightest optical difference between liquid and vapor excepting color, the latter appearing to fill the tube up to the point at which the meniscus disappeared. The color line was not sharply defined. No perceptible amount of solute had precipitated out. The conductivity fell to 1.58 and then, as the temperature fell through about  $0^{\circ}.1$ , again increased slightly.

(2) The color had diffused until it filled the tube to within a short distance of the top. No solute had separated from the solution.

(3) The color had diffused through the whole tube, the color at the top, however, being weaker than lower down the tube.

*Temperature Coefficient of Solution of Potassium Iodide in Methylamine.*

Preliminary experiments upon the properties of methylamine showed it to be a good solvent for a number of metallic iodides and bromides. It also dissolved sugar abundantly. The limited quantity of the solvent at our disposal prevented an extension of these tests. The solution of potassium iodide in methylamine was found to be a fair conductor of electricity as is shown by the results given in the following table:

Weight of solute, 0.0306 gram.

Volume of solvent, 1.9 cc. approximate.

Cell constant, 0.0969.

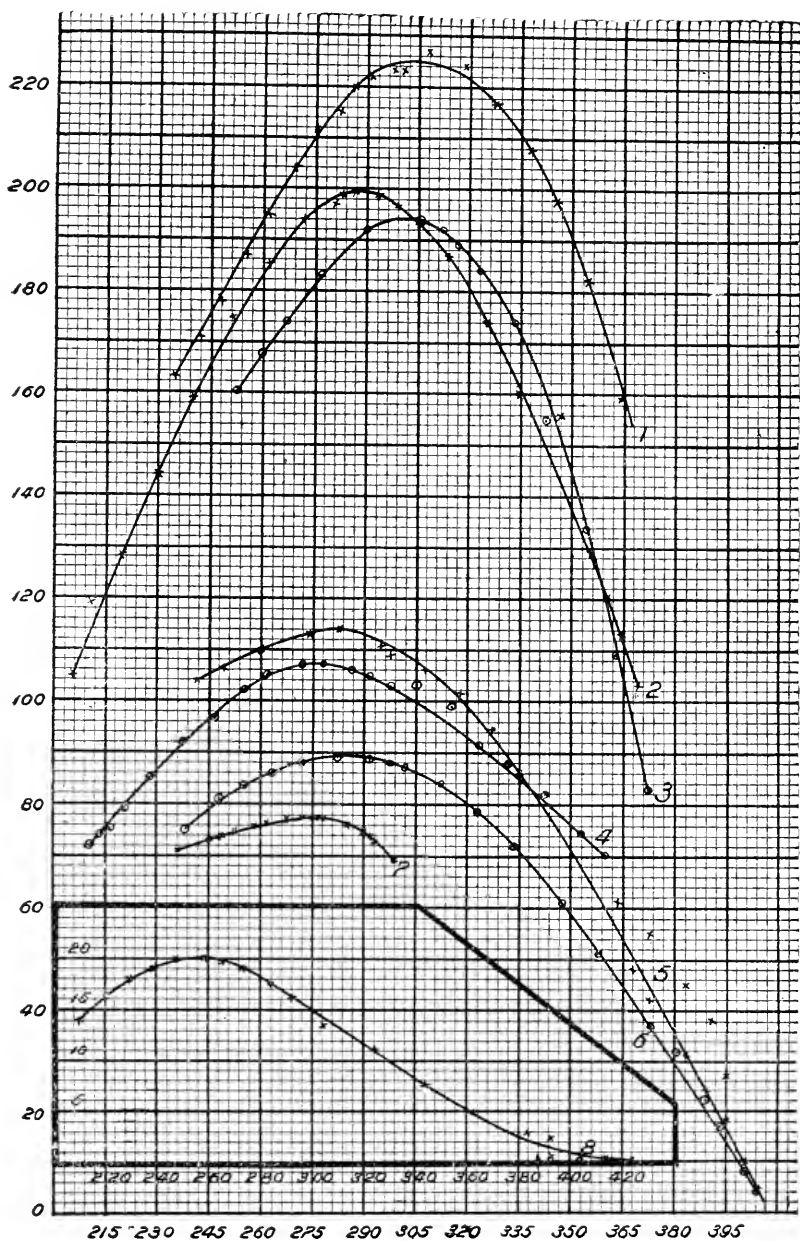
Dilution,  $v$ , 10.31.

T.	$\mu_t$	T.	$\mu_t$
210	14.10	303	13.38
221	15.99	323	11.59
230	17.75	343	7.33
239	19.39	363	4.71
249	20.14	383	3.02
258	20.22	393	2.66
266	19.74	393	0.81
276	18.57	404	0.33
283	17.42	413	0.17
293	15.99	423	0.12

*Temperature Coefficient of Solutions of the Alkali Metals.*

Liquid ammonia acts slowly on metallic sodium in solution with evolution of hydrogen and the formation of sodamide even at 80° below zero. This action between solvent and solute has so far prevented accurate measurements of the temperature coefficient of the solution. In order to obtain an approximate value of the temperature coefficient a solution of sodium was sealed up in a conductivity tube, and placed in a bath of carbon dioxide and ether. After the resistance had become approximately constant the bath was allowed to warm up gradually. This was accompanied by an increase in the conductivity of the solution of about 0.6 per cent per degree. On cooling the tube again the conductivity does not return to its original value. With rising temperature the conductivity continues to increase until the effect of rising temperature is overcome by the removal of metal from solution. The conductivity then falls away until the metal has completely disappeared and the solution takes on the conductivity of the sodamide solution.

For example, one experiment on a solution of sodium gave the following results: At a temperature of 191° absolute, the resistance of the solution in a sealed tube was 8.05 ohms. On slowly warming the tube the resistance fell until a minimum value of 5.92 ohms was reached at 232°. Then as the temperature continued to rise the resistance also increased. On



Graphical Representation of Results.

rapidly cooling to  $220^{\circ}$  the resistance increased to 7.63 ohms. As the bath again warmed up, the resistance fell, passed a minimum, and then increased. After a time the reaction between the metal and the solvent was complete, as was indicated by the entire disappearance of the blue color of the metal solution. The solution then showed the much higher resistance of the solution of sodamide.

Solutions of metallic lithium and potassium also show positive temperature coefficients. These metals also react with the solvent, lithium more slowly and potassium much more rapidly than sodium.

The results of the measurements given in this paper are plotted in the accompanying plate, the temperatures being plotted as abscissae and conductivity as ordinates. It is apparent from the curves that the maxima of all the solutions studied lie above the boiling-point of the solvent and not very far apart. The curves are similar in shape on both sides of the maxima. In the case of those solutes which evidently do not enter into reactions with the solvent, the curves approximate very closely to the parabola. The curves tend toward zero in the neighborhood of  $133^{\circ}$ , the critical temperature of ammonia.

#### *Summary.*

I. Liquid ammonia is a solvent which lends itself to measurements of temperature coefficients of its solutions.

II. Measurements on the solutions of eight electrolytes at increasing temperatures show them all to pass through maxima of conductivity.

III. Solutions in liquid ammonia retain the power of carrying the electric current up to and beyond the critical temperature of the solution.

IV. Solutions of potassium, sodium, and lithium in ammonia exhibit positive temperature coefficients.

V. Methylamine is an electrolytic solvent.

The results so far obtained are but preliminary and are published at this time for the reason that it is not possible for the authors to continue the work together. The investigations will be continued by one of us.



## OBITUARY.

EDOUARD GRIMAUX.

Edouard Grimaux, whose death occurred May 31, 1900, was born in 1835 at Rochefort-sur-Mer. He was originally connected with the marine sanitary corps, but gave up this profession and went to Paris, to study under Wurtz, about the time when the modern theories of chemistry were furnishing a battlefield for the supporters of the new and the old theories. He took his medical degree in 1865, and became assistant in 1872 and adjunct professor in 1874 in the École polytechnique. He succeeded Cahours as Professor, and in 1894 succeeded Fremy in the Académie des Sciences. He was especially interested in the synthetical side of chemistry and was the author of a number of works on chemistry among which were "Equivalents, Atoms, and Molecules"; "Organic Chemistry"; "Inorganic Elementary Chemistry"; "Theoretical Chemistry"; and "Letters, Manuscripts, Private and Collected Papers of Lavoisier." He was removed in 1898, by the Minister of War, from his position as Professor in the École polytechnique, on account of his participation in the Zola affair.

J. E. G.

ADOLF CLAUS.

Any discussion of the interesting, but as yet unsettled, question of the structure of benzene, will necessarily introduce the name of Adolf Claus, whose death occurred May 4th. He suggested and always strongly supported the diagonal formula of benzene and was one of the first to recognize the importance of an understanding of the structural relationship of chemical compounds. He was born in Cassel, June 6, 1838, and, after studying under Kolbe in Marburg and Wöhler in Göttingen, went to Freiburg as assistant to von Babo. His life as a teacher and investigator was spent at this University, where he became Privatdocent in 1863, Associate Professor in 1867, and Professor in 1875. Among the several hundred papers he has published, in conjunction with his students, are those on the relation between oximes and ketones and the isomerism of related compounds, on alkaloids, on the constitution of benzene and naphthalene, on questions of stereoisomerism in a number of cases, on tautomerism, and on many other questions concerning, especially, the aromatic compounds.

J. E. G.



## NOTES.

### *On Krypton.*

In a paper recently communicated to the Berlin Academy of Sciences, Ladenburg and Kruegel give an account of some work done by them on krypton (Chem. News, **81**, 205, 1900). About 3 liters of the residue obtained by evaporating 850 liters of liquid air were used. It was allowed to evaporate slowly, the gas being collected in large gasometers. This large volume of gas (2300 liters) was then freed from oxygen by being passed over heated copper. "From the remaining 120 liters the nitrogen was separated by essentially the methods mentioned by Lord Rayleigh and Ramsay for the isolation of argon." The last traces of nitrogen were removed by sparking over caustic soda with an excess of oxygen. The latter was absorbed by pyrogallol and soda. The gas (3.5 liters) was then dried by means of phosphorus pentoxide and collected in exhausted Ramsay gasometers (Ztschr. physikal. Chem., **28**, 247). By means of liquid air it was condensed to a colorless liquid in which floated small numbers of colorless crystals. The liquid was allowed to boil, the gas being collected in five receivers. The larger part (2.5 liters) boiled at about  $-181.2^{\circ}$ . At  $-153^{\circ}$  the last portions of liquid evaporated, leaving behind the crystals which melted at  $-149^{\circ}$ , and then quickly evaporated. The gas obtained from the boiling liquid was found to be a mixture of krypton and argon, in which the latter predominated. The gas obtained from the crystals gave a strong krypton spectrum, together with some doubtful lines that may have belonged to argon, although the characteristic line of that substance (603.3 mm.) was absent. In comparing the spectra it was found that ten lines of their krypton spectrum were identical with those of the argon spectrum, but several of the fainter argon lines, together with the whole violet end of the argon spectrum do not occur in the krypton spectrum. "One must conclude therefrom that either very little argon or only a constituent part of argon is contained in our krypton."

The density of the gas was found to be 58.81 ( $O = 32$ ) with a probable error of 1 per cent. To control this determination the gas was again sparked with oxygen, the latter was removed by pyrogallol, and the gas was collected over mercury and allowed to stand nearly two days over yellow phosphorus and fused caustic soda. Its density was then found to be 58.67. "Therefrom it follows with certainty that the krypton contained no more oxygen, and since very little argon was

mixed with it, as already inferred from the spectrum examination, one may well consider it as nearly pure. This conclusion is essentially supported by the fact that the gas originated from a crystalline body which doubtless speaks for its not being a mixture." They suggest placing the new gases of the air in the first group in Mendeléef's table, thus: He = 4 before lithium; Ne = 20 before sodium; A = 39 before potassium; and Kr = 59 before copper. "Still this is only a hypothesis which requires further testing."

C. E. W.

*Metallic Calcium and Some of Its Compounds.*

In a recent number<sup>1</sup> of the "Annales de Chimie et de Physique," Moissan describes several methods for the preparation of pure metallic calcium in quantity. As a result of a thorough study of all the methods which had been previously used, and of his experiences with the electric furnace, the author recommends two methods for the preparation of this metal. The first method consists in heating a mixture of anhydrous crystallized calcium iodide and metallic sodium in an iron crucible with a screw top. This was heated for an hour at a low red heat. The condensation of the sodium vapors in the threads of the screw soon made the vessel air-tight and the calcium dissolved in the molten sodium and crystallized when the mass cooled. In order to separate the calcium, the mass was broken up and treated, *in small portions*, with absolute alcohol, which had been freed from air and saturated with pure dry hydrogen, until a portion of the alcohol, when evaporated, left no deposit. It was then washed with anhydrous ether and dried in a current of dry carbon dioxide and hydrogen. In the second method advantage was taken of the fact that calcium oxide, when heated with carbon, is decomposed with the formation of metallic calcium and oxides of carbon. Under ordinary conditions the metallic calcium decomposes the oxides of carbon to form the oxide and carbide; but if an iron tube, of which the part beyond the furnace is surrounded by a lead condenser through which cold water passes, is introduced into one side of the furnace and another tube on the opposite side, for introducing hydrogen, the gases formed can be swept out into the condenser and cooled before they have an opportunity to react upon one another. By this method a mixture of metallic calcium and the hydride is obtained and the pure calcium extracted from this mixture.

The pure calcium is soft and can be cut with a knife like sodium. If entirely free from contact with nitrogen its surface is bright and of the color of silver. It is one of the most ac-

<sup>1</sup> Ann. chim. phys. (7), 18, 289.



tive elements known and combines with all the others except argon. It combines with fluorine at ordinary temperature, and burns in oxygen at  $300^{\circ}$  with the formation of heat sufficient to volatilize the calcium oxide, a phenomenon only observed in the electric furnace. It combines with hydrogen to form the hydride  $\text{CaH}_2$ , and burns brilliantly in the air, forming compounds with both the oxygen and nitrogen. It decomposes water easily and even with incandescence, if it is in the form of powder. It reduces the oxides of boron and silicon, and displaces sodium and potassium from their hydroxides, at red heat. The compound formed by passing pure dry hydrogen over the metallic calcium, which is heated in a glass tube, is especially interesting on account of its great stability. It is not decomposed when heated in a vacuum at  $600^{\circ}$ , in hydrogen to the temperature at which Bohemian glass fuses, nor when heated in air on platinum foil. It, however, burns in pure oxygen at a red heat. No solvent has been found for it. In preparing this substance only small quantities of the calcium can be used at one time, as the heat generated in the action is sufficient to reduce the silicon compounds of the glass, forming a dark layer on the inside of the tube. It decomposes the chlorides of the alkalis, setting the latter free at a red heat, and decomposes oxidizing agents, sometimes accompanied by a violent reaction. It acts on water, liberating hydrogen, of which one-half comes from the water and one-half from the hydride. The compound of the composition  $\text{Ca}_3\text{N}_2$ , which is formed when the calcium is heated in nitrogen, resembles bronze in color. It burns in air with incandescence, and forms the hydride and ammonia when heated in hydrogen. The decomposition with water, to form the hydroxide and ammonia, suggested the possibility of using this method for the preparation of ammonia from the nitrogen of the atmosphere; but under present conditions this method is not practical, although a great step in this direction has been made in this investigation.

A new phosphide,  $\text{Ca}_3\text{P}_2$ , has been obtained by heating calcium phosphate, in the electric furnace under carefully regulated conditions. If the heating is continued too long the phosphide is decomposed with loss of phosphorus. The phosphide melts only in the electric furnace; but dissociates slowly in a vacuum at the temperature at which Bohemian glass melts. If the heating, when the phosphide was formed, was carried far enough, the product of the decomposition with water was pure phosphine, whereas the product formed by insufficient heating generates some liquid phosphine with water.

An interesting fact, which was discovered in the course of

this work, is that pure calcium carbide, made from the pure metal, is perfectly transparent and white, the ordinary appearance being due, as was shown by experiment, to small traces of iron. A determination of the heat of formation of calcium oxide, made with the pure metal, gave the value 145 cal., a figure more in agreement with the facts observed, than the value 131.5 cal., obtained by Thomsen. The value obtained in this case, when compared with those of  $K_2O = +98.2$  cal. and  $Na_2O = +100.9$  cal. furnishes an explanation of the replacement of the alkalis by calcium and suggests the possibility of replacing the lithium in  $Li_2O$ , whose heat of formation is  $+141.2$  cal., a figure also below that of calcium. Experiment showed that lithium could easily be replaced by calcium, thus supporting the theoretical deduction. J. E. G.

#### *On Radioactive Barium.*

Béla v. Lengyel<sup>1</sup> has just published a preliminary notice on the preparation of radioactive barium. Five radioactive elements are now known, uranium, thorium, polonium, radium, and Debierne's element resembling titanium in its chemical properties. Of these, with the exception of uranium and thorium, radium has been most studied. Evidence from its atomic weight and from its spectrum point to its being an element, but the author thinks that such evidence is insufficient. Further, he calls attention to the fact that three new so-called elements, differing only in their radioactivity from well-known elements, have been obtained from one substance, pitchblende.

Such considerations led the author to investigate the question whether radioactive substances contain new elements. In order to answer this question he decided to prepare radium synthetically, if possible. It is evident that if ordinary inactive barium chloride could be transformed into radioactive barium chloride, the problem would be solved. His investigations have led to positive results. He has succeeded in preparing a radioactive barium chloride which possesses all the properties of radium as observed by different investigators.

His method of procedure was as follows: Uranyl nitrate is melted with 2-3 per cent of barium nitrate, the nitric acid driven off as much as possible by heat, and the remaining oxides melted in the electric arc. The melt is dissolved in nitric acid, and the solution concentrated by evaporation, whereupon a large part of the barium separates out as the nitrate. The hot solution is then decanted from the crystals and to it is added three or four times its mass of water. Now

<sup>1</sup> Ber. d. chem. Ges., 33, 1237.

the radioactive barium sulphate is precipitated with sulphuric acid. In this way only a small amount of sulphate is obtained in comparison with the amount of barium nitrate used. Twenty grams of barium nitrate yielded 3-5 grams of the radioactive sulphate contaminated with a large amount of ordinary barium sulphate. From the sulphate the radioactive chloride and carbonate were prepared. The author says that the sulphate is nearly white with a slight yellowish tinge, due probably to a trace of uranium.

The radioactive sulphate, chloride, and carbonate thus prepared produced impressions on photographic plates and rendered gases conductors of electricity.

These experiments are not sufficient to decide the question whether or not radium is an element, but they render its existence doubtful.

The author expects to continue his investigations on this subject.

C. E. C.

#### *On Sulphur Perfluoride, SF<sub>6</sub>.*

Moissan and Lebeau<sup>1</sup> have shown that, when sulphur is introduced into an excess of fluorine in a glass tube over mercury, the sulphur burns with a brilliant flame. After the reaction is over, two gases are found to be present; one of these is insoluble in water, but is absorbed by a solution of potassium hydroxide, while the other is not absorbed either by water or potassium hydroxide, and is decomposed by the vapor of sodium only at the temperature of the boiling-point of the latter.

By repeating the experiment with varying proportions of sulphur and fluorine, it was found that the two fluorides are always formed, but that, when there is an excess of fluorine present, the insoluble gas is formed in larger proportion, sometimes amounting to 90 per cent. The insoluble gas is easily obtained by passing the mixed gases through a solution of potassium hydroxide.

In preparing the mixed fluorides on a large scale, fluorine was passed over sulphur in a horizontal copper tube, and the resulting fluorides were passed into a copper spiral which was cooled down to  $-80^{\circ}$ . This spiral dipped into a glass flask through which was circulated a slow current of pure and dry nitrogen. Under these conditions the two fluorides are completely liquefied. The spiral is then warmed very slowly, and the gases obtained are collected in dry glass flasks. That portion of the gas which comes off first is neglected because it always contains some nitrogen. By repeat-

<sup>1</sup> Compt. rend., 130, 865-871.

ing this process of liquefaction and vaporization all the nitrogen can be removed. The mixture of gases thus obtained is exposed to a concentrated solution of potassium hydroxide for several hours. The remaining gas is dried with fused potassium hydroxide. In order to purify this final product completely, it is cooled down to  $-80^{\circ}$  and allowed to solidify. Then, when it is again converted into a gas, the first portions of gas obtained are neglected because they might contain traces of nitrogen.

The perfluoride of sulphur, which corresponds to the formula  $\text{SF}_6$ , is a colorless, inodorous, tasteless, and incombustible gas. It solidifies at about  $-55^{\circ}$  to a white crystalline mass, which liquefies, and boils at a temperature slightly higher than the temperature of solidification. It is only very slightly soluble in water and in absolute alcohol. Although it is so rich in fluorine, it is remarkable that it is one of the most inert substances, and for the most part its properties resemble those of nitrogen rather than those of the chloride of sulphur. It is not acted on by a concentrated solution of potassium hydroxide, nor is it attacked by copper oxide at dull red heat. It is not decomposed by a fusing mixture of potassium hydroxide and lead chromate. Heated in a closed tube to a temperature at which the glass softens, it undergoes no change, the glass remaining unattacked by it.

When subjected to the influence of the electric spark of a Ruhmkorff coil capable of giving a spark 8–10 cm. long in air, the perfluoride of sulphur is partly decomposed. In one experiment there were obtained 23.30 per cent of a gas soluble in water with the deposition of silica; 44.36 per cent of a gas soluble in potassium hydroxide; and 33.33 per cent of undecomposed perfluoride. After sparking the perfluoride for two hours and thirty-five minutes, 11.64 per cent of it still remained undecomposed.

Heated with hydrogen, the perfluoride of sulphur suffers no change, but when a mixture of these two gases is sparked, hydrofluoric acid and hydrogen sulphide are formed, and these substances then react on each other in the presence of the glass to form sulphur, hydrofluosilicic acid, and silica.

Fluorine does not react on the perfluoride of sulphur, as is evident from its method of preparation, nor do chlorine nor the vapor of iodine act on it at dull red heat.

Oxygen acts on the perfluoride of sulphur only under the influence of a strong electric spark. The perfluoride is then entirely decomposed. If the spark is not strong, an oxyfluoride of sulphur is formed, which is less rapidly decomposed by water than thionyl fluoride.

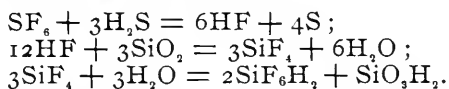
Fused sulphur has no effect on this new gas, though it is converted into lower fluorides when heated in a sealed tube with sulphur. These lower fluorides attack glass, yielding sulphur dioxide and silica.

The vapor of selenium decomposes the perfluoride of sulphur with the formation of silicon fluoride and the anhydrides of selenious and sulphurous acids.

Phosphorus, arsenic, boron, silicon, and carbon at low red heat have no effect on the perfluoride of sulphur.

Sodium attacks the perfluoride only at the temperature of its boiling-point. Calcium and magnesium react with it at red heat. Copper and silver have no effect on it at the temperature of fused glass.

Hydrochloric acid gas does not react with the perfluoride of sulphur when heated in a sealed tube to the temperature at which glass softens, nor does ammonia gas in the cold or at high temperatures affect it. Hydrogen sulphide, when heated with it, yields sulphur, hydrofluosilicic and silicic acids according to the following equations :



In a later paper Moissan and Lebeau<sup>1</sup> give an account of their experiments undertaken for the purpose of determining the density and the composition. The results are very satisfactory.

The following summary given by the authors is helpful :

By the action of an excess of fluorine on sulphur a new gas, the perfluoride of sulphur of the formula  $\text{SF}_6$ , is formed. This gas is one of the heaviest known, its density being 5.03. Its composition establishes the hexavalence of sulphur. As a compound of fluorine it corresponds to sulphuric anhydride,  $\text{SO}_3$ . It is curious to observe that two such active substances as sulphur and fluorine should combine to form a gas which is not attacked by molten potassium hydroxide nor by sodium at its point of fusion.

This new fluoride of sulphur is totally different from the chlorides of sulphur, and it shows once more that in chemistry it is well to beware of analogies. Fluorine, although it belongs to the family of the halogens, possesses a character of its own, by virtue of which it sometimes forms unexpected combinations.

C. E. C.

<sup>1</sup> Compt. rend., 130, 984-988.

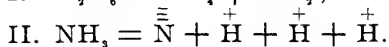
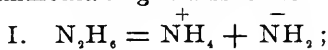
## REPORT.

### *Ammonia a Weak Tribasic Acid.*

A series of papers has just appeared by Frenzel,<sup>1</sup> working in Göttingen with Nernst, in which the conclusion has been reached that ammonia is a weak tribasic acid. The conductivity of liquid ammonia was first studied. The values which had been obtained by Goodwin using commercial liquid ammonia dried over lime were  $1.392 \times 10^{-4}$  and  $1.688 \times 10^{-4}$ . Frenzel distilled commercial liquid ammonia and dried the gas over lime, then recondensed the gas and determined the conductivity of the liquid. He found  $1.1 \times 10^{-5}$ , a value about one-twelfth that obtained by Goodwin.

He then prepared pure liquid ammonia from pure ammonium chloride and lime, washed the gas in a strong solution of potassium hydroxide to remove any carbon dioxide, and dried it by passing it over soda-lime and finally over potassium copper oxide. The gas was then liquefied in a vessel surrounded by solid carbon dioxide and ether. The conductivity of the liquid ammonia prepared in this way was found in two determinations to be:  $1.33 \times 10^{-7}$ , and  $1.47 \times 10^{-7}$ , a value very much smaller than that which had been previously obtained.

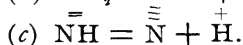
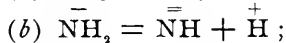
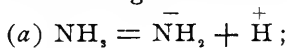
The author then raises the question, what are the ions into which pure ammonia dissociates in order to give any conductivity whatsoever? There are two possible ways in which a molecule of ammonia might dissociate:



The first method is only a possibility, but is very improbable from what we know about dissociation in general.

The second method would lead to the, at first sight, astonishing conclusion that ammonia is a weak tribasic acid, since, wherever we have hydrogen ions we have acid properties, and when a molecule yields three hydrogen ions it is a tribasic acid.

These are simply suggestions. Before they can have much value they must be tested experimentally. If ammonia is a weak tribasic acid it would not break down at once into a nitrogen anion and three hydrogen cations, but like all weak acids would dissociate in stages. We should have:

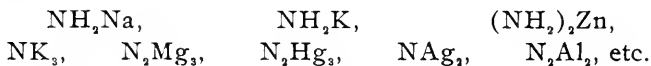


<sup>1</sup> Ztschr. Elektrochemie, 6, 477, 485, 493.

To test this, Frenzel made use of the polarization method. Every ion present in a solution will manifest itself by an irregularity in the polarization curve. It then only remained to work out the polarization curve of pure liquid ammonia, and see whether there were any irregularities corresponding to the three stages of dissociation represented above. To make the liquid ammonia a better conductor a little potassium nitrate, or ammonium chloride, or some other soluble salt was added to it. Every polarization curve showed these irregularities, which were practically independent of the nature of the salt used. These fell in the regions of 0.48, 0.66, and 0.78 volts, and since it was the anode polarization which was studied, it must have been due to the anions  $\text{NH}_2^-$ ,  $\text{NH}^-$ , and  $\text{N}^{3-}$ . That these irregularities in the curves are due to the ammonia and not to the dissolved salt is made extremely probable by the fact that they always appeared, whatever the nature of the salt added to the ammonia.

The conclusion that ammonia is a weak tribasic acid is thus, apparently, substantiated by the experiments of Frenzel. He also succeeded in showing that hydrogen separates directly upon the cathode, but this line of evidence is not as strong as that first considered.

This conclusion naturally grates upon our preconceived ideas regarding ammonia, but the author points out that there are a number of well-known compounds of the metals with ammonia which would show that ammonia can act as an acid. Thus :



and this list might be considerably extended.

Here we have ammonia playing the rôle of an acid, forming well-characterized substances with the strongly metallic elements.

Whatever may be our opinion in reference to the conclusions which should be drawn from this work, it is quite clear that our older definitions of acids and bases must give place to new and more comprehensive ones. We seem forced to the physical-chemical definitions of acids and bases. An acid is a substance which yields hydrogen ions under any conditions. Wherever we have hydrogen ions we have acid properties, and, conversely, wherever we have acid properties we have hydrogen ions. Similarly, hydroxyl is the characteristic ion of bases. A substance may be an acid, yielding hydrogen ions under one set of conditions, and a base, yielding hydroxyl

ions under different conditions. This seems to be the case with ammonia.

H. C. J.

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## REVIEWS.

LEXIKON DER KOHLENSTOFF-VERBINDUNGEN. By M. M. RICHTER. Second edition. Hamburg and Leipzig: Leopold Voss. 1899.

The second edition of this valuable work, the first edition of which appeared in 1883, will be welcomed by those who have had occasion to consult the early edition, which has been left far behind in the forward march of the science. Some idea of the great activity in chemistry in the last twenty years can be obtained from a consideration of the material contained in these two editions. In the edition of 1883 about 16,000 substances were classified, while the present edition contains about 67,000, the third edition of "Beilstein" containing about 57,000. The system of arrangement is the same as in the former edition, but a new feature, the percentage composition of about 20,000 formulæ, has been added. The value of this system of identifying chemical substances and the thorough manner in which the system has been worked out has been recognized by the editors of a number of the most important chemical journals, and this feature has been incorporated in their indexes. A copy of this work should be accessible to every chemist.

J. E. G.

JAHRESBERICHT ÜBER DIE FORTSCHRITTE DER CHEMIE UND VERWANDTER THEILE ANDERER WISSENSCHAFTEN. Begründet von J. LIEBIG und H. KOPP. Unter Mitwirkung namhafter Fachgenossen herausgegeben von G. BODLÄNDER. Für 1893. Erstes Heft. Braunschweig: Vieweg. 1900. 10 Marks.

The old "Jahresbericht" has had a hard time of it for a good many years, and it has seemed as though it would never be up to date. Recently, Dr. von Buchka has given up the editorship and Professor Bodländer has taken up the work. The publishers now promise the volumes for 1893, 1896, and 1897 in the course of the year 1900, and they express the hope that in a short time the other missing volumes will be finished. This is certainly much to be desired, for, although we have the "Centralblatt" and the "Jahrbuch der Chemie," we still need a carefully edited Jahresbericht, such as the old Liebig and Kopp has generally been.

The first number (Heft), which has just come to hand, numbers 320 pages and deals with general and physical chemistry. The work appears to have been carefully done and to be worthy of the "Jahresbericht."

I. R.



# AMERICAN CHEMICAL JOURNAL

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## THE ACTION OF CARBON DIOXIDE ON THE BORATES OF BARIUM.

By H. N. MORSE AND D. W. HORN.

In Volume 10 of THIS JOURNAL, one of us, with W. M. Burton, published a method for the separation and determination of boric acid. The proposed procedure was as follows: If the acid is in solution, the liquid containing it is made slightly alkaline with caustic potash and evaporated in a porcelain dish to a volume of 10 or 12 cc. If, on the other hand, the material is insoluble, *e. g.* a silicate, about 4 grams of solid potassium hydroxide are fused in a nickel crucible until the liquid mass becomes tranquil. After cooling and solidifying, the pulverized mineral is spread over the surface, and the crucible is heated for two hours just high enough to keep the hydroxide in molten condition, the contents being stirred from time to time with a stout platinum wire, which is allowed to remain in the crucible. The soluble matter is separated from the insoluble by extraction with water, filtration, and washing upon the filter. The filtrate is then evaporated to the small volume mentioned above. If the mineral contains iron, the contents of the crucible are treated with not less than 400 cc. of water, and heated for some time in order to insure

the precipitation of all of the ferric hydroxide. The filtrate is then evaporated as in other cases.

The solution of alkaline borate is treated with tropæolin (better with methyl orange), and then, under a covering glass, with sulphuric acid until an acid reaction is obtained. The covering glass is washed into the dish, and the liquid cautiously brought to the neutral condition with very dilute caustic potash. The solution, which contains in the free state only boric, carbonic, and silicic acids, and whose volume should not exceed 20 cc., is dried by stirring into it anhydrous copper sulphate. The pulverized dry material is transferred to a straight calcium chloride tube, in the bottom of which a plug of cotton wool has been placed, and extracted with absolute alcohol.

In this manner it was found practicable effectually to separate boric acid from the bases and acids with which it is usually associated, and this was regarded by the authors of the process as the most, and in fact the only, important feature of their contribution. When the question of determining the acid in the alcoholic solution arose, they were confronted with the well-known difficulties of the methods at that time available for getting boric acid in solution into weighable form. The procedure which they adopted was free from some of the objections to earlier processes, and gave, as far as it was tested, very satisfactory results. It was as follows: The alcoholic extract was drawn from the filter into a flask containing a measured volume of a standard solution of barium hydroxide. The excess of the hydroxide was converted into carbonate by passing a current of carbon dioxide through the liquid. The contents of the flask were then transferred to a weighed platinum dish, evaporated to dryness, and heated to constant weight by rapidly moving the flame of a triple burner over the outer surface of the dish. Knowing the weight of the barium in the mixture of salts, and that of its carbonate, if all of it were precipitated by the carbon dioxide, the weight of the boric acid could be calculated by the following proportion:

$$\begin{array}{l} \text{Mol. wt. B}_2\text{O}_3\text{—mol. wt. CO}_2 : \text{mol. wt. B}_2\text{O}_3 :: \\ \text{wt. found—theoretical wt. BaCO}_3 : \text{wt. B}_2\text{O}_3. \end{array}$$

The essential weakness of basing the estimation of the acid, after its separation, upon such a calculation is perfectly obvious, and the fact that analytical errors are magnified three-fold in the results was not overlooked by the authors of the process. It was believed, however, that with careful work quite as high a degree of accuracy could be attained by this method as by the others then in use.

The process was tested by its authors by determining the boric acid in three substances: borax glass, datholite from Bergen Hill, and tourmaline from Pierrepont. It was then placed in the hands of two of the best analysts in the laboratory, with the request that they also try it upon some of the same materials. All of the results were satisfactory.

In Volume V (series 4) of the American Journal of Science, L. C. Jones describes some experiments with an aqueous solution of boric acid which was treated with an excess of barium hydroxide, then with carbon dioxide, and afterwards dried, and the residue heated with a view to securing constant weight. The results exhibit great lack of uniformity, and differ very widely in nearly every case—sometimes in one direction and again in the other—from the quantities which should have been obtained if the residues consisted only of the metaborate and carbonate of barium. The author concludes that the weights vary with the degree of the ignition; and this he supposes to be due to the action of the carbon dioxide upon the metaborate, as well as upon the excess of hydroxide. His view appears to be that carbon dioxide precipitates a portion of the barium from the metaborate, liberating boric acid which is lost, in part, during the subsequent evaporation. On igniting the residue afterwards, the portion of free acid which was not lost during the evaporation displaces carbon dioxide with reformation of barium borate, and the net result must be positive or negative according to the degree of the completeness of this reaction. If all of the free acid is reconverted into metaborate, there should be a deficit just equal to the weight of the boric acid which was lost during evaporation. Again, on fusing together weighed quantities of barium metaborate and carbonate, it was found that the prod-

uct weighed less than the original mixture, showing that the two salts react with liberation of carbon dioxide.

"These results," the author says, "were so surprising in the light of the experience of Morse and Burton that the question of the possibility of breaking up by carbon dioxide the barium metaborate already formed was put to the test directly." Accordingly, he prepared a known weight of the salt, dissolved it in hot water, passed carbon dioxide through the solution, evaporated to dryness, ignited, and weighed. There was an increase in weight, showing "that carbon dioxide had been absorbed, while a corresponding amount of boric acid had not been volatilized." "After passing in carbon dioxide and igniting, the increase in weight was 0.028 gram representing the gas absorbed less the boric acid volatilized."

Thinking that possibly the amount of the carbon dioxide might be so regulated "as to leave the metaborate practically unattacked....carbon dioxide was passed above the stirred solution until no further precipitate formed upon the surface, the barium present being in excess of that required to form a metaborate." On ignition an apparent loss of 0.0412 gram of boric acid was observed. Concerning this experiment, the author says: "The variation of this result from the theory shows that under these conditions the metaborate is not unaffected by the carbon dioxide, *the loss being due, of course, to the escape of boric acid.*" In the succeeding experiment phenolphthalein was added to a solution of boric acid which had been treated with an excess of barium hydroxide, and the current of carbon dioxide was discontinued when the color disappeared. The dried residue was repeatedly ignited, with the result that the apparent error varied between +0.0438 gram after the first heating, and -0.013 gram after the seventh. Finally, it was proved that, by continuously removing the boric acid in the form of the methyl ether, the metaborate of barium can be completely decomposed by carbonic acid.

Near the beginning of his article, after giving a synopsis of the method proposed by Morse and Burton, the author says: "I have made a study of this method applied to pure boric acid, but have been unable to obtain results similar to

those of Morse and Burton." At the close, he adds: "In view of the facts which I have described, it is difficult to see under what conditions Morse and Burton prevented the excessive action of carbon dioxide and obtained in their analytical method the excellent results which they record."

We must question the correctness of the author's statement, that he has "made a study of this method;" for he appears to us to have failed to satisfy the first requirement of a genuine study of the same, in that he has neglected to adhere to the essential conditions under which the original work was done. He employed *aqueous solutions* only, and yet seems to assume that he was dealing with the meta salt, notwithstanding the presence of an excess of barium hydroxide, whereas it is highly probable that a compound containing a larger proportion of the base was formed. An experiment which may be cited as evidence to this effect is recorded by P. Berg,<sup>1</sup> who found that when barium hydroxide is added to an aqueous solution of boric acid in such quantity that the ratio of BaO to B<sub>2</sub>O<sub>3</sub> is as 1.5 to 1, the precipitate which is first formed is dissolved, and that, too, by virtue of the additional half molecule of BaO.

On the other hand, the authors of the method in question worked with *strong alcoholic solutions* and, therefore, were dealing, without doubt, with the metaborate; since it has been shown by Berg<sup>2</sup> that in alcoholic solutions the meta salt is precipitated, whether the ratio of B<sub>2</sub>O<sub>3</sub> to BaO is as 1 : 1, 1 : 1.5, 1 : 2, 1 : 3, or 1 : 3.5.

Again, in the aqueous solutions containing an excess of barium hydroxide, *i. e.*, more than is required for the formation of the meta salt, the borates (whatever their composition may have been) must have been to a great extent dissolved, in which condition they would be acted upon rapidly by the carbon dioxide; while in the strong alcoholic solutions employed by Morse and Burton, the metaborate is only very slightly soluble. The great mass of the salt was therefore in a condition in which it could be acted upon only slowly by the gas. According to their original directions, the volume of the

<sup>1</sup> Ztschr. anal. Chem., 16, 26.

<sup>2</sup> *Loc. cit.*, 27.

aqueous solution of barium hydroxide which is employed in a determination of boric acid is about 25 cc. Into this is drawn the solution of boric acid in absolute alcohol, which, together with the alcohol used in washing, has a volume of from 90–100 cc. Hence the liquid which is afterwards treated with carbon dioxide for the purpose of precipitating the barium from the excess of hydroxide is—roughly estimated—at least a 78 per cent alcohol. The solubility of the metaborate in a 75 per cent alcohol is given as 1 part in 55,000. 125 cc. of the 78 per cent liquid should not, therefore, contain more than 2 mgms. of the metaborate in solution when treated with carbon dioxide, and even this small quantity should not be attacked by the gas until after the excess of the hydroxide has been neutralized. At all events, it seems highly improbable that the undissolved metaborate should be seriously attacked by the carbon dioxide during the short time required to neutralize the excess of hydroxide. If the treatment with the gas were carried beyond the neutralization of the hydroxide, the metaborate would doubtless suffer to some extent; but the immediate result would not be, as supposed by Jones, the liberation of boric acid, but rather the formation of a still more acid borate. He speaks repeatedly of the *liberation* of boric acid when carbon dioxide is passed into a solution of the metaborate of barium, and ascribes certain considerable deficits in weight to a loss of this free acid during evaporation. But one of his own experiments appears to indicate that the product of the action of the gas upon a borate is a more acid salt and not the free acid; for he states that when he passed carbon dioxide into a solution containing 1 gram of boric acid and 0.15 gram of barium hydroxide, “no precipitate could be obtained.” This must mean that carbon dioxide is incapable, under the conditions, of decomposing the most acid of the borates.

An evaporating solution containing, as some of those of the author probably did, a very acid borate of barium, the acid carbonate of the same, and perhaps free carbonic acid, quickly loses the free and semicombined carbonic acid, and this loss should be attended by the simultaneous formation of a borate holding in combination a larger proportion of barium. If, as

he supposes, these solutions also contain free boric acid, and, as he states, "the division of the base between boric acid and carbonic acid falls under the principle of mass action," the rapid loss of the latter during evaporation should be followed by an equally rapid neutralization of the former. Hence, even if some of the boric acid is actually in the free state, at the beginning of the evaporation, it cannot long remain free, but must recombine with the barium as the equilibrium is disturbed by the disappearance of the carbonic acid; and the acid borates thus formed, though possibly not wholly stable, should not lose acid during evaporation as readily as does an aqueous solution of boric acid in the absence of a base. It is difficult for us to understand, in view of "the principle of mass action," how any of the boric acid should be actually liberated until all of the barium carbonate had been converted into the acid salt. This, however, would involve very prolonged treatment with the gas.

These considerations led us to think that Jones, in ascribing certain deficits in weight to loss of boric acid by volatilization, had misinterpreted the cause of the results which seemed to him so strange. It appeared to us improbable that, under the conditions, any weighable quantity of the acid could be lost in that way. On the other hand, the following simple hypothesis, which is based on well-known facts, would account for all the phenomena observed by him.

1. Having treated his boric acid in aqueous solutions with an excess of barium hydroxide (*i. e.* more than was necessary to form the meta salt) he had to deal, not as he appears to suppose, with the metaborate, but with a salt containing a larger proportion of the base—possibly with  $(\text{BaO})_2\text{B}_2\text{O}_5$ .

2. On conducting carbon dioxide into the liquid, any excess of hydroxide would be neutralized, and then the borate would be attacked with precipitation of barium carbonate and formation of an acid borate; and whether a mixture of neutral and acid borates, or the metaborate, or possibly a still more acid salt would be produced, would depend on the length of the exposure to the gas, as would, likewise, the initial weight of the dried residue. If the treatment with carbon dioxide were stopped before all of the neutral borate had been

converted into the meta salt, the residue would be too light—that is, for a mixture of carbonate and metaborate; if it were carried just to this point (which would happen only by chance), the expected weight would be obtained, while any more prolonged action of the gas would give a residue having too great a weight.<sup>1</sup>

3. On heating the residue to a temperature sufficiently high, the acid borates—the metaborate as well as the more acid salts—would attack the carbonate with formation of less acid borates and expulsion of carbon dioxide. This reaction—with the consequent decline in weight—would continue until all of the acid had been converted into the neutral—or most basic—borate of barium, when the weight would become constant.

The decomposition of carbonates by acid borates at high temperatures is, of course, a very familiar reaction; and it affords the most obvious explanation of the continuous loss in weight which was observed by Jones when he subjected his mixtures of borate and carbonate to repeated ignitions. That the metaborate will decompose the carbonate of barium was shown by one of Jones's own experiments. The assumption that any portion of the deficits in weight was due to loss of boric acid by volatilization appears to be unnecessary.

He is clear, both as to the fact that carbon dioxide decomposes the meta salt in aqueous solution, and that the metaborate decomposes the carbonate of barium at high temperatures; but his evident conviction that his solutions, before treatment with carbon dioxide, contained the metaborate, despite the excess of barium hydroxide, and, therefore, that his conditions were comparable with those of Morse and Burton, is, we believe, without justification. If they contained a more basic borate, as it is morally certain they did, it is obvious that Jones could not have obtained the expected weight except by accident. He had two chances of obtaining a residue consisting of metaborate and carbonate only: first,

<sup>1</sup> It is to be remarked in this connection, however, that a too great initial weight of the residue does not necessarily indicate that the action of the carbon dioxide has gone beyond the formation of the metaborate, *i. e.*, has resulted in the production of a still more acid salt; since the metaborate, when formed in the presence of water, is hydrated, and the first heating of the residue may not suffice for its complete dehydration.



to stop the treatment with carbon dioxide when his more basic salt had been converted into the metaborate ; second, having passed beyond this point, to discontinue the subsequent ignition when the more acid borate had been reconverted into the meta salt at the expense of the carbonate. There is, however, no possible means of determining when either of these goals has been reached. That phenolphthalein will not serve for the identification of the first is clear from Jones's experiment No. VII, where, on the first weighing, a surplus of 0.0438 gram was obtained, notwithstanding the fact that " the current of gas was stopped when the color of the indicator disappeared."

It may be urged that even if Morse and Burton had the metaborate in insoluble condition, and it had not been sensibly attacked during the treatment with carbon dioxide, nevertheless, in the subsequent attempt to heat the dried residue to constant weight, the metaborate must have attacked the carbonate. It has since then come to light that some caution must be exercised in this part of the manipulation. In the original description of the method, it was simply stated that the residue was heated to constant weight over a triple burner. The practice then, and on the few occasions when the process has since been used, was to hold the burner in the hand and rapidly play the flame over the platinum dish in order to secure as uniform a temperature of the contents as possible. The object in using a triple burner was not to obtain a very high temperature, which is not necessary, but, rather, to employ a flame large enough to keep the whole dish hot. No difficulty was experienced, when the heating was conducted in this manner, in quickly obtaining constant and correct weights. Nevertheless, it must be admitted, the authors of the method did not at that time suppose that the temperature at which the meta salt will attack the carbonate is so low as it has since been found to be. The temperatures employed by Jones were evidently far above those to which Morse and Burton heated their mixtures of metaborate and carbonate.

The authors of the present paper proposed at the outset to undertake a somewhat elaborate investigation of the action of carbonic acid on the borates of barium under different condi-

tions, and of the action of the acid borates upon the carbonate of barium at high temperatures. In the midst of the work, however, the laboratory in which the investigation was in progress, also all of the materials and apparatus employed in connection therewith, were destroyed by fire, compelling them to postpone for a considerable time the further prosecution of the work in this direction. Enough, nevertheless, had been accomplished to justify certain conclusions, and we give our results now, notwithstanding the incompleteness of the investigation, because we were originally delayed in taking it up far beyond the time when the communication of Jones should have received attention.

The first question which we undertook to examine bears upon the method of Morse and Burton. It is possible, if the alcoholic liquid containing the insoluble metaborate and the excess of the hydroxide of barium is treated with carbon dioxide much longer than is necessary for the neutralization of the latter, that a sensible quantity of the boric acid might be lost in the form of ethyl borate during the subsequent evaporation. We determined to test this point under much severer conditions than those which prevail when the process is carried out according to the original directions. To this end a solution of crystallized boric acid in absolute alcohol (1 cc. containing 0.007 gram  $B_2O_3$ ) and an aqueous solution of barium hydroxide (1 cc. containing 0.0224 gram  $BaO$ ) were made. A tubulated retort, with its neck near the small end bent to an angle and raised somewhat above the horizontal, was attached to a condenser. The glass stopper was replaced by a cork carrying a tube for the introduction of gas. Measured quantities of the solutions of acid and hydroxide and an additional quantity of alcohol were brought together in the retort and treated for a considerable time with carbon dioxide; and then, without interrupting the current of gas, the alcohol was distilled off and the distillate tested by the flame reaction for boric acid. More alcohol was added to the residue in the retort and distilled off as before, the treatment with carbon dioxide being continued throughout the time occupied in the distillation. This retreatment of the residue with alcohol with subsequent distillation in a current of carbon dioxide was

three times repeated with each mixture. Previously we had determined what, for us, was the lower limit of the flame reaction for boric acid, and had found that we could just discern the green color when 1 part of the acid was dissolved in about 14,200 parts of absolute alcohol. The results of four experiments of the kind described are given below. The letters *a*, *b*, *c*, and *d* signify 1st, 2nd, 3rd, and 4th distillations :

	Volume of distillate. cc.	Concentration of distillate. Per cent.	Character of flame reaction.
I. <i>a</i>	....	72.0	negative
<i>b</i>	....	82.0	"
<i>c</i>	....	92.0	traces
<i>d</i>	....	96.0	"
II. <i>a</i>	52.0	68.0	negative
- <i>b</i>	50.0	64.5	"
<i>c</i>	54.0	68.0	"
<i>d</i>	52.0	....	"
III. <i>a</i>	50.5	75.6	negative
<i>b</i>	52.0	74.6	"
<i>c</i>	51.1	72.6	"
<i>d</i>	50.5	....	"
IV. <i>a</i>	51.0	74.0	negative
<i>b</i>	51.5	69.5	"
<i>c</i>	53.0	64.5	"
<i>d</i>	51.0	71.0	"
V. <i>a</i>	51.2	75.0	negative
<i>b</i>	51.2	73.0	"
<i>c</i>	51.2	74.0	doubtful
<i>d</i>	50.9	72.0	"

In experiments I. to IV. portions of the distillates were burned directly, and it will be noted that only when the alcoholic concentration rose to 92 per cent, or higher, did the distillates contain a quantity of boric acid which could be detected by the flame when the test is thus applied. In experiment V., on the other hand, the distillates which gave no green flame when burned were treated with a small quantity of caustic potash and evaporated to dryness, and the flame test was then applied to the residues after treating them with 0.5 cc. of absolute alcohol and a little concentrated sulphuric acid.

The quantities of boric acid which were carried over appear to have been very minute, notwithstanding the distillation in

a current of carbon dioxide ; and this fact renders it probable that a loss of acid in consequence of etherification is not to be feared when the evaporation is carried out in the manner prescribed by Morse and Burton ; that is, in the absence of the gas and only after a moderate treatment with it. Nevertheless, it was our intention to return to the subject at a later period for the purpose of securing positive evidence upon this point.

In one of Jones's experiments, boric acid was treated with an excess of barium hydroxide (*i. e.* with more than enough to form the metaborate), and the mixture with carbon dioxide until no further precipitate formed on the surface of the stirred liquid. The weight fell short 0.0412 gram, " the loss being due, of course, to the escape of boric acid," the author says. As we have already explained, such a loss of the acid by volatilization seemed to us improbable under the conditions. A better explanation of the deficit appeared to be that Jones either had not carried the treatment with carbon dioxide far enough to convert all of his more basic borate into the meta salt ; or, having carried it to this point or beyond, that he had afterwards heated the material so high that a more basic salt than the metaborate had been formed at the expense of the carbonate. We therefore undertook to ascertain whether, under conditions analogous to those described by Jones, there is an appreciable loss of boric acid.

Accordingly, some powdered turmeric root was extracted, first with water and then with 95 per cent alcohol, and from the alcoholic extract test-papers were prepared which were afterwards properly protected from the light.

Aqueous solutions containing minute known quantities of boric acid were tested with the papers with a view to determining the limit of the reaction, the solutions having first been treated with just enough hydrochloric acid to produce a distinct acid reaction with methyl orange. When a test was to be made, an equally dilute solution of hydrochloric acid in pure water was employed for comparison. A paper was cut in halves, one half was dipped in the acidified solution of boric acid, and the other for the same length of time in the dilute hydrochloric acid. Both strips were then dried upon a

warmed glass plate and the effects compared. When a paper failed to show the reaction after the first dipping and drying, it was redipped and dried again and again. In this way a distinct reaction could be obtained in solutions so dilute that a single treatment failed to reveal a trace of acid. The coloring-matter, however, gradually concentrated in the highest part of the wet portion of the strip rendering an indefinite repetition of the process impracticable. In this way we were able to detect 1 part of the acid in 59,000 parts of water by a single dipping, and 1 part in 143,000 by dipping four or five times. The turmeric test for boric acid in water appears, therefore, to be much more delicate than that of the flame in alcoholic solutions.

In the following group of experiments, the same apparatus was employed as before, but the current of carbon dioxide, which in the earlier experiments had been conducted through the retort during the evaporation, was replaced by one of heated air. This was done in order to facilitate the evaporation upon the water-bath. An aqueous solution of boric acid containing 0.00636 gram  $B_2O_3$  per cc., and one of barium hydroxide containing 0.02538 gram  $BaO$  per cc., were brought together in the retort, the latter being in excess of the quantity required to form the metaborate. Phenolphthalein was added and carbon dioxide conducted through the liquid for a short time longer than was necessary to destroy the color. The current of carbon dioxide was then replaced by one of air, which was heated before entering the retort by passing it through a hot porcelain tube filled with fragments of the same material. In this way a comparatively rapid distillation could be effected upon the water-bath. The whole of the water was distilled out of the retort and collected in the receiver. The conditions and results are stated below :

	Volume of liquid in the retort. cc.	Ratio of $BaO : B_2O_3$ .	Number of times necessary to dip paper to detect acid.	Possible amount of $B_2O_3$ in the distillate. Gram.
VI.	13.77	2 : 1	3	0.00012
VII.	14.84	2 : 1	3-5	0.00013
VIII.	14.36	2 : 1	3	0.00013
IX.	14.72	2 : 1	4	0.00010
X.	22.35	4 : 1	4	0.00016

It is assumed, in making the estimates given in the last column, that since 1 part of the acid can be detected in 59,000 parts of water by once dipping, and 1 part in 143,000 parts by dipping four times, 1 part in 87,000, and 1 part in 115,000 could be detected by dipping twice and three times, respectively.

The quantity of boric acid found in the distillates is so minute that one may well question whether we have not to do here with a mechanical transportation of the finely divided liquid in suspension above a mass of liquid through which a gas is breaking its way.

Three similar experiments (Nos. XI., XII., and XIII.) were made with alcoholic solutions, but the work in this direction was not completed for the reason already explained. An alcoholic solution of boric acid and a water solution of barium hydroxide were introduced into the retort, and enough alcohol added to bring the concentration of the whole up to 50 per cent. As before, the mixture was treated with a little phenolphthalein, then with carbon dioxide, and finally distilled to dryness with the aid of a current of hot air. The distillate was tested in the manner previously described with turmeric paper. The attempt to determine the limit of sensibility of the reaction in alcoholic solutions was unfinished; but it appeared probable, from the few experiments which were made, that a smaller amount of boric acid can be detected in 50 per cent alcohol by the turmeric test than can be found in absolute alcohol by the flame reaction. The dipping of the papers, however, cannot be repeated as many times in an alcoholic, as in an aqueous, solution, owing to the solubility of the coloring-matter in the former.

	Volume of liquid in the retort. cc.	Ratio of BaO : B <sub>2</sub> O <sub>3</sub> .	Number of times necessary to dip paper to get reaction.
XI.	15.75	2 : 1	3
XII.	31.48	2 : 1	2
XIII.	24.48	4 : 1	2

In the second part of our work, we proposed to study the effect of different temperatures upon the weights of mixtures of borates and carbonate, such as are produced when boric

acid is treated with an excess of barium hydroxide and afterwards, more or less thoroughly, with carbon dioxide; and to determine also the effect of exposing these mixtures, after heating, in an atmosphere containing carbon dioxide. It was to be expected, in view of the known conduct of other similar mixtures, that, if the more acid borates (including the meta salt) decompose the carbonate at high temperatures, at lower temperatures the gas would be reabsorbed, and that certain ranges of temperature might be found through which acid borates of definite composition would be stable, notwithstanding the presence of barium carbonate or of carbon dioxide. As far as the matter in controversy is concerned, it was our object to find the temperature at which it was presumed a mixture of the metaborate and the carbonate of barium is stable, or, rather, the temperature at which it becomes unstable.

Solutions of boric acid in alcohol and of barium hydroxide in water were employed, the latter being always in excess of the quantity required to form the meta salt. The character of the treatment with carbon dioxide is described in connection with each experiment.

*Experiment XIV.*

Weight of BaO = 0.2745 gram = 0.35315 gram BaCO<sub>3</sub>.

“ “ B<sub>2</sub>O<sub>3</sub> = 0.09834 gram = 0.17418 gram H<sub>2</sub>BO<sub>3</sub>.  
 = 0.12362 gram HBO<sub>2</sub> = 0.31419 gram  
 BaO.B<sub>2</sub>O<sub>3</sub>.

Excess of BaO = 0.0586 gram = 0.07547 gram BaCO<sub>3</sub>.

Weight of mixture, if consisting of BaO.B<sub>2</sub>O<sub>3</sub> and BaCO<sub>3</sub>,  
 only, = 0.38959 gram.

Volume of the mixed solutions = 42.24 cc.

The material was evaporated to dryness on a water-bath under an uninterrupted current of carbon dioxide.

	Weight of residue. Gram.	Change of weight. Gram.	Variation from wt. of BaO. BaO <sub>3</sub> + BaCO <sub>3</sub> . Gram.
1. Dried 1½ hours on water-bath	0.44427	.....	+0.05468
2. Exposed cold, after moisten- ing, to CO <sub>2</sub> for 48 hours, and then heated on water- bath	0.44426	0.0000	+0.05468
3. Heated 40 minutes over triple burner	0.38591	-0.05835	-0.00368
4. Heated 40 minutes over triple burner	0.37699	-0.00892	-0.01260
5. Heated 15 minutes over triple burner	0.37428	-0.00271	-0.01531
6. Heated 15 minutes over triple burner	0.37278	-0.00150	-0.01581
7. Heated 15 minutes over triple burner	0.37152	-0.00126	-0.01807
8. Heated 5 minutes over triple burner	0.37031	-0.00121	-0.01928

The results recorded above are similar to some of those obtained by Jones. The weights in the beginning are greater than those calculated for a mixture of carbonate and metaborate only, but on successive strong ignitions they decline, rapidly at first, and then more slowly. The excess of weight observed when the residue was heated only to the temperature of the water-bath shows one of two things: 1. That the metaborate, if it was formed at all, had been robbed of some of its barium by the carbon dioxide with formation of a more acid salt; or, 2. That the metaborate took up and retained water of crystallization at the temperature of the bath. If the residue contained only carbonate and the meta salt and the latter had appropriated 2 molecules of water, the calculated weight of the mixture would have been 0.44027 gram instead of 0.44427 gram, as it was found to be. The difference of only 4 mgms. between the two weights suggests the possibility that the excess of weight was not due to the decomposition of the metaborate by the gas, but to the presence of water in the former. It will be shown by a later experiment that when carbon dioxide, either dry or saturated with water vapor, is passed over dry metaborate of barium, the gas is not



absorbed at any temperature between that of the air and a red heat. This fact, however, proves nothing as to what may occur when the salt is more or less in the dissolved condition.

The fact that no increase in weight was observed when (2) the residue, after the first drying, was again moistened and exposed for forty-eight hours in an atmosphere of carbon dioxide, appears to show that the gas had produced its maximum effect, under the conditions, during the first evaporation. Nevertheless, the action of the carbon dioxide could not have proceeded so far as to convert all of the barium into carbonate; for, if the residue had consisted of  $\text{BaCO}_3 + \text{H}_2\text{BO}_3$ , the weight would have been 0.52733 gram; if of  $\text{BaCO}_3 + \text{HBO}_2$ , it would have been 0.47677 gram; while, if the mixture had consisted of  $\text{BaCO}_3 + \text{B}_2\text{O}_3$ , we should have had a weight of 0.45149 gram. The last supposition is, of course, inadmissible in view of the low temperature to which the residue was heated. Since all of these weights are higher than that obtained, the obvious conclusion is that our mixture, when first weighed, could not have consisted of carbonate and free boric acid, but rather that it consisted either of carbonate and metaborate containing water, or of carbonate and a more acid borate than the meta salt. The only alternative explanation of the excess of weight involves a considerable loss of boric acid by volatilization.

Experiment XIV. was duplicated except that the residue, after the first evaporation, was moistened with water and again dried on the bath in an atmosphere of carbon dioxide, and then heated for ten minutes over a single burner before weighing. The results were similar to those of XIV. The first weight was too large by 0.0156 gram, but, after five successive ignitions over a triple burner, it was too small by 0.0207 gram for a mixture of carbonate and metaborate. These losses at high temperatures are ascribed without much hesitation to the expulsion of carbon dioxide, since it is proved by a later experiment that the gas is liberated under analogous conditions.

In order to determine beyond question the composition of the residues and the nature of the overweight which is observed under conditions similar to those already described, it

will be necessary to supplement experiments like XIV. and XV., and others to be described hereafter, by still others in which the volatile products are collected from stage to stage and weighed. We had expected to do this, and shall utilize the first opportunity to carry out our plan.

### Experiment XVI.

Weight  $\text{BaO} = 0.3144 \text{ gram} = 0.40457 \text{ gram } \text{BaCO}_3$ .

“  $\text{B}_2\text{O}_3 = 0.08019 \text{ gram} = 0.14203 \text{ gram } \text{H}_3\text{BO}_3 =$   
 $0.1008 \text{ gram } \text{HBO}_2 = 0.25546 \text{ gram } \text{BaO} \cdot \text{B}_2\text{O}_3$ .

Excess of  $\text{BaO} = 0.13838 \text{ gram} = 0.25611 \text{ gram } \text{BaCO}_3$ .

Weight of mixture, if consisting of  $\text{BaO} \cdot \text{B}_2\text{O}_3$  and  $\text{BaCO}_3$  only,  $= 0.43428 \text{ gram}$ .

Volume of mixed solutions ( $31.87 \text{ cc. } \text{Ba}(\text{OH})_2$  and  $11.46 \text{ cc. } \text{H}_3\text{BO}_3$ )  $= 43.33 \text{ cc.}$

The vessel containing the mixed liquids was placed under a bell-jar which was connected at the top with a carbon dioxide generator, and allowed to stand for an hour. It was then placed on a water-bath, the liquid evaporated, and the apparently dry residue heated for four hours. Carbon dioxide was not passed into the dish during the evaporation.

	Weight of residue. Gram.	Change of weight. Gram.	Variation from wt. of $\text{BaO} \cdot \text{B}_2\text{O}_3$ + $\text{BaCO}_3$ . Gram.
1. First weighing	0.54003	.....	+0.10575
2. Stood $1\frac{3}{4}$ hours in the air	0.54140	+0.00137	+0.10712
3. Heated $\frac{1}{2}$ hour on water-bath	0.53919	-0.00221	+0.10491
4. Stood $14\frac{1}{2}$ hours in the air	0.53998	+0.00079	+0.10630
5. Heated $\frac{1}{4}$ hour on water-bath	0.53811	-0.00187	+0.10383
6. Stood 1 hour in the air	0.53958	+0.00147	+0.10530
7. “ 6 days “	0.54078	+0.00120	+0.10650
8. Heated $3\frac{1}{2}$ hours at $100^\circ$ in air-bath	0.53821	-0.00257	+0.10393
9. Stood $7\frac{3}{4}$ hours in the air	0.53921	+0.00100	+0.10493
10. Heated $3\frac{1}{8}$ hours at $100^\circ$ in air-bath	0.53510	-0.00411	+0.10082
11. Stood $25\frac{1}{2}$ hours in the air	0.53815	+0.00305	+0.10387
12. Heated 1 hour at $100^\circ$ in air- bath	0.53370	-0.00445	+0.09942
13. Stood 4 hours in the air	0.53719	+0.00349	+0.10291
14. Heated 1 hour at $110^\circ$	0.53253	-0.00466	+0.09825

	Weight of residue. Gram.	Change of weight. Gram.	Variation from wt. of $\text{BaO} \cdot \text{B}_2\text{O}_3$ + $\text{BaCO}_3$ . Gram.
15. Stood 4 hours in the air	0.53554	+0.00301	+0.10126
16. Heated 1 hour at $110^\circ$	0.53109	—0.00445	+0.09681
17. Stood $1\frac{1}{2}$ hours in the air	0.53423	+0.00314	+0.09995
18. Heated 2 hours at $110^\circ$	0.53173	—0.00250	+0.09745
19. Stood $3\frac{3}{4}$ hours in the air	0.53403	+0.00230	+0.09975
20. Heated $4\frac{1}{4}$ hours at $110^\circ$	0.53380	—0.00023	+0.09952
21. Stood $1\frac{1}{2}$ hours in the air	0.53462	+0.00082	+0.10034

In the preceding table the material is stated to have stood for various periods of time in the air, and the weights given are those found at the close of these periods; in every case, however, several intermediate weighings were made and the exposure was not discontinued until the increase in weight in the air became insignificant.

The results are believed to have some bearing on the question of the actual liberation of boric acid in consequence of the action of carbon dioxide on the mixture. If all of the barium had been converted into carbonate, and all of the boric acid had been liberated as  $\text{H}_3\text{BO}_3$ , the combined weight of the two would have been 0.5466 gram, which is only 0.0066 gram greater than the first weight found after the last heating upon the water-bath (No. 5). This fact might be construed, at first sight, as evidence of such a reaction, but the subsequent conduct of the material when heated in the air-bath shows that free boric acid ( $\text{H}_3\text{BO}_3$ ) could not have been present; for, after heating three and one-half hours at  $100^\circ$  (No. 8), the change in weight from the last heating upon the water-bath (No. 5) was —0.0001 gram, which, of course, has no significance whatever. On subsequently heating to the same temperature for four and one-sixth hours in all (Nos. 10 and 12), the loss amounted to 0.00451 gram; but on standing in the air for four hours (No. 13), all of this, except 1 mgm., was recovered. Again, on heating to the higher temperature of  $110^\circ$  (Nos. 14, 16, 18, and 20) for various periods, amounting altogether to eight and a quarter hours, the loss from the last heating at  $100^\circ$  amounted only to 0.0044 gram; and after each heating (except the final one when the exposure was only one

and a half hours), the material showed a tendency to recover in the air what it had lost in the bath. These slight losses and their subsequent recovery in the air indicate the presence of a salt containing water, and disprove, we think, the presence of any weighable quantity of the free acid; since boric acid,  $\text{H}_3\text{BO}_3$ , is said to lose water at  $100^\circ$  and to pass at that temperature into the meta acid,  $\text{HBO}_2$ . It is perhaps useless to speculate seriously as to what hydrated salt was present, but it is to be noted that either  $\text{BaOB}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , or  $\text{BaO}(\text{B}_2\text{O}_3)_2 \cdot 7\text{H}_2\text{O}$ —the superfluous barium being in the form of carbonate—would have given weights very nearly equal to those which were obtained. The first would have given the weight 0.53184 gram, and the second the weight 0.53193 gram, while the weight obtained after the last heating to  $110^\circ$  was 0.5338 gram. These coincidences, however, we do not regard as having any particular weight since, doubtless, still other possible hydrated acid salts would satisfy the conditions equally well.

### Experiment XVII.

Weight  $\text{BaO} = 0.51673$  gram  $= 0.66492$  gram  $\text{BaCO}_3$ .

“  $\text{B}_2\text{O}_3 = 0.09871$  gram  $\text{B}_2\text{O}_3 = 0.17484$  gram  $\text{H}_3\text{BO}_3$ .  
 $= 0.12409$  gram  $\text{HBO}_2 = 0.31446$  gram  $\text{BaO} \cdot \text{B}_2\text{O}_3$ .

Excess of  $\text{BaO} = 0.30006$  gram  $= 0.38703$  gram  $\text{BaCO}_3$ .

Weight of mixture, if consisting of  $\text{BaO} \cdot \text{B}_2\text{O}_3$  and  $\text{BaCO}_3$  only,  $= 0.70149$  gram.

Volume of mixed solutions (36.00 cc.  $\text{Ba}(\text{OH})_2$  and 14.13 cc.  $\text{H}_3\text{BO}_3$ )  $= 50.13$  cc.

The liquid was evaporated to a small volume on the water-bath, and then treated for one-half hour with carbon dioxide without removal from the bath. The current was discontinued and the residue evaporated to dryness.

	Weight of residue. Gram.	Change of weight. Gram.	Variation from wt. of $\text{BaO} \cdot \text{B}_2\text{O}_3$ + $\text{BaCO}_3$ . Gram.
1. First weighing	0.72571	.....	+0.02422
2. Stood $1\frac{1}{2}$ hours in the air	0.72652	+0.00081	+0.02503
3. Heated $3\frac{1}{2}$ hours at $100^\circ$ in air- bath	0.72291	-0.00361	+0.02142
4. Stood $7\frac{1}{4}$ hours in air (7 inter- mediate weighings)	0.72581	+0.00290	+0.02432
5. Heated $3\frac{1}{2}$ hours at $100^\circ$ in air- bath	0.72300	-0.00281	+0.02151
6. Stood $5\frac{1}{2}$ hours in the air (6 intermediate weighings)	0.72412	+0.00112	+0.02263
7. Heated 1 hour at $100^\circ$ in air- bath	0.72175	-0.00237	+0.02026
8. Stood $4\frac{1}{2}$ hours in the air (5 intermediate weighings)	0.72275	+0.00100	+0.02126
9. Heated 1 hour at $110^\circ$	0.71984	-0.00291	+0.01835
10. Stood 4 hours in the air (5 in- termediate weighings)	0.72147	+0.00163	+0.01998
11. Heated 1 hour at $110^\circ$	0.71886	-0.00261	+0.01737
12. Stood $1\frac{1}{2}$ hours in the air (3 intermediate weighings)	0.72183	+0.00297	+0.02034
13. Heated 2 hours at $110^\circ$	0.71750	-0.00433	+0.01601
14. Stood $3\frac{3}{4}$ hours in the air (5 intermediate weighings)	0.72172	+0.00422	+0.02023

The material exhibited very much the same conduct in this as in the preceding experiment. When heated for seven and two-thirds hours at  $100^\circ$ , it lost in the former case from the first weighing 0.00633 gram and regained in the air 0.00349 gram, the net loss at  $100^\circ$ , with subsequent exposure, being 0.00294 gram; while in the latter case, with a heating of eight hours, with subsequent exposure, the net loss was 0.00296 gram. The net changes in weight at  $110^\circ$ , from the last weights at  $100^\circ$ , were, in the former instance, +0.0007 gram, and in the latter, -0.00003 gram. The inference might perhaps be drawn from this similarity of conduct that the same salt was formed in both instances, notwithstanding the different manner in which the two mixtures were treated with carbon dioxide. If all of the boric acid were present in the residue in Experiment XVII. as  $\text{BaOB}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , the weight should have been 0.72693 gram, which differs only 0.00172 gram from

the first weight obtained after removing the dish from the water-bath. However, the supposition that a metaborate containing only 1 molecule of water was formed would by no means account for all the weight obtained in Experiment XVI. It is therefore concluded that either different acid salts were formed, or, if the same salt was produced, it differed in the two cases in its degree of hydration.

### Experiment XVIII.

Weight BaO = 0.68545 gram = 0.88203 gram BaCO<sub>3</sub>.

“ B<sub>2</sub>O<sub>3</sub> = 0.10148 gram = 0.18013 gram H<sub>3</sub>BO<sub>3</sub>.

= 0.12756 gram HBO<sub>3</sub> = 0.32423 gram BaOB<sub>2</sub>O<sub>3</sub>.

Excess of BaO = 0.46271 gram = 0.59551 gram BaCO<sub>3</sub>.

Weight of mixture, if consisting of BaOB<sub>2</sub>O<sub>3</sub> and BaCO<sub>3</sub>, only, = 0.91963 gram.

Volume of mixed solutions (31.26 cc. Ba(OH)<sub>2</sub> and 14.45 cc. H<sub>3</sub>BO<sub>3</sub>) = 45.71 cc.

Carbon dioxide was passed over the material during the entire time of the evaporation upon the water-bath, and the residue was heated to 120° for two and a half hours before weighing.

	Weight of residue. Gram.	Change of weight. Gram.	Variation from wt. of BaOB <sub>2</sub> O <sub>3</sub> + BaCO <sub>3</sub> . Gram.
1. First weighing	0.94014	.....	+0.02051
2. Heated 3½ hours at 120° (3 intermediate weighings)	0.93961	—0.00053	+0.01998
3. Heated 12½ hours at 110° (2 intermediate weighings)	0.94395	+0.00434	+0.02432
4. Heated 60½ hours at 150° (11 intermediate weighings)	0.93057	—0.01238	+0.01094
5. Heated 9 hours at 175°	0.92560	—0.00497	+0.00597
6. Heated 23 hours at 175°	0.92109	—0.00451	+0.00146
7. Heated 3½ hours at 175°	0.92296	+0.00187	+0.00333
8. Heated 9½ hours at 175°	0.92305	+0.00009	+0.00342

### Experiment XIX.

Weight BaO = 0.68685 gram = 0.88383 gram BaCO<sub>3</sub>.

“ B<sub>2</sub>O<sub>3</sub> = 0.10106 gram = 0.17938 gram H<sub>3</sub>BO<sub>3</sub> =

0.12703 gram HBO<sub>3</sub> = 0.32252 gram BaOB<sub>2</sub>O<sub>3</sub>.

Excess of BaO = 0.46503 gram = 0.59849 gram BaCO<sub>3</sub>.

Weight of mixture, if consisting of  $\text{BaOB}_2\text{O}_3$  and  $\text{BaCO}_3$ , only, = 0.92127 gram.

Volume of mixed solutions (31.41 cc.  $\text{Ba}(\text{OH})_2$  and 14.39 cc.  $\text{H}_3\text{BO}_3$ ) = 45.80 cc.

The treatment with carbon dioxide was the same as in XVIII.; that is, the gas was passed over the material during the entire time occupied in the evaporation upon the water-bath. The residue, as in the case of No. XVIII., was heated to  $120^\circ$  for two and a half hours before weighing.

	Weight of residue. Gram.	Change of weight. Gram.	Variation from wt. of $\text{BaO} \cdot \text{B}_2\text{O}_3$ + $\text{BaCO}_3$ . Gram.
1. First weighing	0.93846	.....	+0.01719
2. Heated $1\frac{3}{4}$ hours at $120^\circ$	0.93230	-0.00616	+0.01103
3. Heated 2 hours at $120^\circ$ (2 weighings)	0.93306	+0.00076	+0.01179
4. Heated $12\frac{1}{2}$ hours at $110^\circ$ (2 weighings)	0.93501	+0.00195	+0.01374
5. Heated $88\frac{3}{4}$ hours at $150^\circ$ (11 weighings)	0.92515	-0.00986	+0.00388
6. Heated 44 hours at $175^\circ$ (4 weighings)	0.91964	-0.00551	-0.00163

Nos. XVIII. and XIX. are duplicates. Both residues exhibit a tendency to lose weight slowly when the temperature is raised from  $120^\circ$  to  $150^\circ$  and  $175^\circ$ , and to gain weight when the temperature is lowered from  $120^\circ$  to  $110^\circ$ . At  $175^\circ$  both approach the theoretical weight for a mixture of  $\text{BaOB}_2\text{O}_3$  and  $\text{BaCO}_3$ . The calculated weight for a mixture of  $\text{BaOB}_2\text{O}_3 \cdot \text{H}_2\text{O}$  and  $\text{BaCO}_3$  was, for No. XVIII., 0.94578 gram, for No. XIX., 0.94732 gram; while the first weights found were 0.94014 gram and 0.93846 gram, respectively. The differences are 0.00564 gram and 0.00718 gram.

#### Experiment XX.

Weight  $\text{BaO}$  = 0.56113 gram = 0.72217 gram  $\text{BaCO}_3$ .

"  $\text{B}_2\text{O}_3$  = 0.12592 gram = 0.27638 gram  $\text{BaO}$ , if  
 $\text{BaOB}_2\text{O}_3$  is formed, = 0.40230 gram  $\text{BaOB}_2\text{O}_3$ .

Excess of  $\text{BaO}$  = 0.28475 gram = 0.3664 gram  $\text{BaCO}_3$ .

Weight of mixture, if consisting of  $\text{BaOB}_2\text{O}_3$  and  $\text{BaCO}_3$ , only, = 0.7687 gram.

Volume of mixed solutions (20.39 cc.  $\text{Ba}(\text{OH})_2$  and 16.90 cc.  $\text{B}_2\text{O}_3$ ) = 37.29 cc.

The liquid was evaporated to a small volume on the water-bath and then treated, still hot, for fifteen minutes with carbon dioxide. During the latter period the contents of the dish were stirred with a platinum rod. The drying of the residue was completed on an iron plate.

	Weight of residue. Gram.	Change of weight. Gram.	Variation from wt. of $\text{BaOB}_2\text{O}_3 +$ $\text{BaCO}_3$ . Gram.
1. Heated to redness over burner	0.75126	.....	—0.01744
2. " " " " "	0.74996	—0.0013	—0.01874
3. Stood in the air 18 hours (2 weighings)	0.76632	+0.01636	—0.00238
4. Stood in the air 48 hours	0.77439	+0.00807	+0.00569
5. " " " " $50\frac{1}{2}$ "	0.77410	—0.00029	+0.00540
6. Heated to redness over burner	0.75361	—0.02049	—0.01509
7. " " " " "	0.75605	+0.00244	—0.01265
8. " " " " "	0.75418	—0.00187	—0.01452
9. Moistened with water, saturated with $\text{CO}_2$ , and heated cautiously over burner	0.76669	+0.01251	—0.00201
10. Repeated treatment No. 9	0.77036	+0.00367	+0.00166

The results obtained in No. XX. show that when carbon dioxide has been lost in consequence of excessive heating, and the material is exposed to the air, there is a recovery of weight (Nos. 3 and 4), which must, of course, be due to the absorption of water or carbon dioxide, or of both. The increase in weight ceases after a time (No. 5), but the stable weight reached in this manner somewhat exceeds that calculated for a mixture of  $\text{BaOB}_2\text{O}_3 + \text{BaCO}_3$ . When the residue is moistened with water, treated with carbon dioxide, and afterwards heated more cautiously, as in Nos. 9 and 10, its weight again approaches that estimated for a mixture of metaborate and carbonate.

#### Experiment XXI.

Weight  $\text{BaO}$  = 0.29846 gram = 0.38406 gram  $\text{BaCO}_3$ .

"  $\text{B}_2\text{O}_3$  = 0.06682 gram = 0.14777 gram  $\text{BaO}$ , if

$\text{BaO.B}_2\text{O}_3$  is formed = 0.21488 gram  $\text{BaO.B}_2\text{O}_3$ .

Excess of  $\text{BaO}$  = 0.15069 gram = 0.19394 gram  $\text{BaCO}_3$ .



Weight of mixture, if consisting of  $\text{BaO.B}_2\text{O}_3$  and  $\text{BaCO}_3$ , only, = 0.40882 gram.

Volume of mixed solutions (10.85 cc.  $\text{Ba}(\text{OH})_2$  and 8.97 cc.  $\text{H}_3\text{BO}_3$ ) = 19.82 cc.

The liquid was evaporated to a small volume on the water-bath and then treated for fifteen minutes with carbon dioxide (as in XX.). The dried residue was heated to redness and weighed.

	Weight of residue. Gram.	Change of weight. Gram.	Variation from wt. of $\text{BaO.B}_2\text{O}_3$ + $\text{BaCO}_3$ . Gram.
1. First weighing	0.40294	.....	—0.00588
2. Heated to redness	0.40076	—0.00218	—0.00806
3. Stood in air 20 hours (2 weighings)	0.40817	+0.00741	—0.00065
4. Stood in air 65 hours	0.41108	+0.00291	+0.00226
5. " " " 67½ "	0.41198	+0.00090	+0.00316
6. " " " 71½ "	0.41088	—0.00110	+0.00206
7. Moistened with water, treated with $\text{CO}_2$ , using phenol- phthalein, and heated to red- ness	0.41952	+0.00864	+0.01070
8. Heated to redness	0.41563	—0.00389	+0.00681
9. " " "	0.41187	—0.00376	+0.00305
10. " " "	0.41040	—0.00147	+0.00158
11. " " "	0.40939	—0.00101	+0.00057
12. Repeated treatment No. 7	0.41783	+0.00844	+0.00901
13. " " " Nos. 7 and 12	0.41280	—0.00503	+0.00398
14. Heated to redness	0.41012	—0.00268	+0.00130
15. Heated longer and higher than in No. 14	0.40366	—0.00646	—0.00516
16. Heated to redness	0.40198	—0.00168	—0.00684
17. " " "	0.40164	—0.00034	—0.00718
18. Stood 2½ hours in air (6 weighings)	0.40623	+0.00459	—0.00259
19. Stood 2½ hours in air (2 weighings)	0.40751	+0.00128	—0.00131
20. Stood 1½ hours in the air	0.40800	+0.00049	—0.00082
21. " 3 " " " "	0.40899	+0.00099	—0.00017
22. " 24 " " " "	0.41037	+0.00138	+0.00155
23. Stood over $\text{CaCl}_2$ 2 hours	0.40983	—0.00054	+0.00101
24. " " " 7 "	0.40969	—0.00014	+0.00087
25. " " " 9 "	0.40947	—0.00022	+0.00065
26. " " " 24 "	0.40941	—0.00006	+0.00059

	Weight of residue. Gram.	Change of weight. Gram.	Variation from wt. of BaO.B <sub>2</sub> O <sub>3</sub> + BaCO <sub>3</sub> . Gram.
27. Heated to redness	0.40495	-0.00446	-0.00387
28. " " "	0.40352	-0.00143	-0.00530
29. " " "	0.39733	-0.00619	-0.01149
30. " " "	0.39746	+0.00013	-0.01136
31. " " "	0.39709	-0.00037	-0.01173
32. " " "	0.39722	+0.00013	-0.01160
33. " " "	0.39732	+0.00010	-0.01150
34. " " "	0.39624	-0.00108	-0.01258
35. Repeated treatment Nos. 7, 12, and 13	0.41112	+0.01488	+0.00230
36. Repeated treatment Nos. 27 to 33 (7 weighings)	0.39948	-0.01164	-0.00934
37. Stood 15 hours in the air	0.40898	+0.0095	+0.00016
38. " 37 " " " " (2 weighings)	0.40931	+0.00033	+0.00049
39. Stood 22 hours in the air	0.40959	+0.00028	+0.00077
40. " 39 " " " "	0.41045	+0.00086	+0.00163
41. " over CaCl <sub>2</sub> 3 hours	0.40939	-0.00106	+0.00057
42. " " " 6½ "	0.40948	+0.00009	+0.00066

Our experiments XXII. to XXVI. inclusive, were similar to XXI., except that the manner of treating the mixed liquids with carbon dioxide was varied to some extent. In most of them phenolphthalein was added to the liquid and the treatment with the gas discontinued when the color disappeared. The results only confirm the obvious conclusions to be drawn from the data already presented, and we therefore omit them. These conclusions are :

1. At a full red heat the meta salt attacks the carbonate with expulsion of carbon dioxide.

2. The temperature at which a mixture of the metaborate and the carbonate of barium is stable and which is still sufficiently high to insure the dehydration of the former appears to be just under a red heat.

3. If a mixture of the metaborate and carbonate has been heated too high, *i. e.* so high that some of the latter has been decomposed with formation presumably of a more basic borate, the lost weight is restored by exposing the material to the air. The weight gained through the exposure is slightly greater than is required to bring the mixture up to the theo-

retical weight, but the excess is lost when the mixture is placed in a desiccator. The experiment of heating the material, after treatment with carbon dioxide, until the weight fell below that calculated for a mixture of metaborate and carbonate, and then of exposing it in the air until the weight became very nearly constant, and, finally, of removing the slight excess of weight by placing the material over calcium chloride or sulphuric acid, was many times repeated and always with a satisfactory degree of success except in two cases. In these it was suspected that, while some portions of the material had been heated high enough to decompose the carbonate, other portions had not reached the temperature required for the complete dehydration of the metaborate; for it was observed that the weights gained in the air on these occasions far exceeded the calculated deficits.

4. If the material which has been reduced below its theoretical weight by prolonged ignition is moistened with water and then treated with carbon dioxide, it quickly gains not only the weight required for a mixture of metaborate and carbonate, but considerable besides. Whether the excess of weight so acquired is due to the formation of more acid borates or to the acquisition of water by the meta salt, or to both causes, can be ascertained only by collecting and determining the compounds which are volatilized when the product is again heated.

In Experiments XXVII. to XXX., inclusive, an iron bath surrounded by asbestos board and a mercury thermometer for high temperatures were employed. By placing three burners under the bath, the temperature could be raised at times somewhat beyond the range of the thermometer, *i. e.*, above  $550^{\circ}$ ; at other times, however, with the same arrangement of lamps, the temperature would not rise above  $460^{\circ}$  or  $470^{\circ}$ .

*Experiment XXVII.*

Weight  $\text{BaO} = 0.38103 \text{ gram} = 0.49030 \text{ gram } \text{BaCO}_3.$

“  $\text{B}_2\text{O}_3 = 0.09200 \text{ gram} = 0.20194 \text{ gram } \text{BaO}, \text{ if converted into } \text{BaOB}_2\text{O}_3 = 0.29394 \text{ gram } \text{BaOB}_2\text{O}_3.$

Excess  $\text{BaO} = 0.17909 \text{ gram} = 0.23045 \text{ gram } \text{BaCO}_3.$

Weight of mixture, if consisting of  $\text{BaOB}_2\text{O}_3$  and  $\text{BaCO}_3$  only, = 0.52439 gram.

Volume of mixed solutions (14.93 cc.  $\text{Ba}(\text{OH})_2$  and 12.37 cc.  $\text{H}_3\text{BO}_3$ ) = 27.2 cc.

The mixed solutions were treated with phenolphthalein and then, cold, with carbon dioxide for five minutes after the color had disappeared. After evaporation to dryness on the water-bath, the residue was heated in the air-bath previously mentioned.

	Weight of residue. Gram.	Change in weight. Gram.	Variation from wt. of $\text{BaOB}_2\text{O}_3$ + $\text{BaCO}_3$ . Gram.
1. Heated 5 hours at $450^\circ$ - $470^\circ$	0.55756	.....	+0.03317
2. Stood $1\frac{1}{4}$ hours in the air	0.56011	+0.00255	+0.03572
3. Heated $11\frac{1}{4}$ hours over 3 burn- ers (3 weighings)	0.54682	-0.01329	+0.02243
4. Heated 9 hours over 3 burn- ers	0.53219	-0.01463	+0.00780
5. Heated 6 hours over 3 burners	0.52244	-0.00975	-0.00195
6. Stood 3 hours in the air	0.52703	+0.00460	+0.00265
7. Stood 24 hours in the air	0.52817	+0.0011	+0.00378
8. Stood 48 hours over $\text{H}_2\text{SO}_4$	0.52761	-0.00056	+0.00322
9. Heated 7 hours over 3 burners	0.52177	-0.00584	-0.00262
10. Stood $4\frac{3}{4}$ hours in the air	0.52586	+0.00409	+0.00147
11. " 8 hours in the air	0.52637	+0.00051	+0.00198
12. " 24 hours in the air	0.52685	+0.00048	+0.00246
13. " 36 " over $\text{H}_2\text{SO}_4$ (3 weighings)	0.52638	-0.00047	+0.00199
14. Heated 9 hours at $450^\circ$ - $475^\circ$	0.52497	-0.00141	+0.00058
15. Stood 24 hours in the air	0.5261	+0.00113	+0.00171
16. " 48 " over $\text{H}_2\text{SO}_4$	0.52597	-0.00013	+0.00158
17. Heated out of bath to redness	0.51584	-0.01013	-0.00855
18. Stood 6 hours over dilute so- lution of KOH	0.53680	+0.02096	+0.01241
19. Stood $66\frac{1}{2}$ hours over $\text{H}_2\text{SO}_4$	0.52577	-0.01103	+0.00138
20. " $68\frac{1}{2}$ " " " "	0.52574	-0.00003	+0.00135
21. Heated 7 hours at $450^\circ$ - $470^\circ$	0.52359	-0.00215	-0.00080
22. Stood in air 1 hour	0.52405	+0.00046	-0.00034
23. Heated 4 hours at $460^\circ$ - $470^\circ$	0.52480	+0.00075	+0.00041
24. Stood 1 hour in air	0.52485	+0.00005	+0.00046
25. Heated 9 hours in bath over 3 burners	0.52733	+0.00248	+0.00294
26. Stood $\frac{1}{4}$ hour in air	0.52754	+0.00021	+0.00315
27. Heated out of bath over burner	0.52180	-0.00574	-0.00259

	Weight of residue. Gram.	Change in weight. Gram.	Variation from wt. of BaOB <sub>2</sub> O <sub>3</sub> + BaCO <sub>3</sub> . Gram.
28. Heated 2 hours at 450°-470°	0.52517	+0.00337	+0.00078
29. " 1 hour " 450°-470°	0.52537	+0.00020	+0.00098
30. " " " " 450°-470°	0.52554	+0.00017	+0.00115
31. " out of bath over burner	0.51902	-0.00652	-0.00537
32. Heated 1 hour at 450°-460°	0.52225	+0.00323	-0.00214
33. " " " " 440°-460°	0.52365	+0.00140	-0.00074
34. " " " in bath over 3 burners and allowed to cool in the bath	0.52431	+0.00066	-0.00008
35. Repeated No. 34	0.52446	+0.00015	+0.00007
36. " " "	0.52459	+0.00013	+0.00020
37. " " "	0.52480	+0.00021	+0.00041
38. " " "	0.52496	+0.00016	+0.00057
39. " " "	0.52511	+0.00015	+0.00072

Experiments XXVIII., XXIX., and XXX. resembled XXVII. very closely, and the results were so similar to those recorded under that number that they need not be given here in detail. In general, it was found difficult, by heating in our bath, to bring the too great initial weight of the material down to that calculated for a mixture of metaborate and carbonate, though in one case (No. XXX.) this was accomplished by heating in the bath for three hours over three burners. The temperature on this occasion, however, rose so high that the thermometer was removed. The conduct of the material in the air, after having been heated, appeared to be contradictory. At times the weight would rise in the air from slightly below the theoretical to several milligrams above it, and only a part of the excess would disappear over sulphuric acid; while at other times, the gain in the air would carry the weight only slightly above the theoretical, and then the loss in the desiccator would just about suffice to reduce it to that calculated for a mixture of metaborate and carbonate. We have only a provisional explanation to offer for this conduct. It was noticed in some of the earlier experiments, in which the material had been much more highly heated and the weight greatly reduced thereby, that, on exposure to the air, it gained only enough to carry its weight a little above the normal, and

that nearly all of the excess was lost in the desiccator. And on comparing the later experiments with the earlier, it was found that the same thing occurred in those instances in which the weight of the material had previously been reduced several milligrams below the theoretical weight. This led us to suspect that the temperature at which complete dehydration occurs and that at which the metaborate begins to attack the carbonate do not lie very far apart, and that a salt which has not been completely dehydrated is capable of taking on more water from the air, while one which has been heated high enough to expel all of the water is comparatively indifferent to atmospheric moisture. In these later experiments, as in the earlier ones, there was no difficulty in obtaining nearly theoretical results by heating the material until its weight was considerably below that calculated for a mixture of carbonate and metaborate, then exposing it to the air until the weight became nearly constant, and finally drying in a desiccator, or heating to a temperature approaching  $500^{\circ}$ . From this it appears probable that the more basic borate which is formed at high temperatures is decomposed at ordinary temperatures by the carbon dioxide of the air and reconverted into the metaborate and carbonate. A similar absorption of carbon dioxide takes place when material whose weight has been reduced below the normal amount is reheated in the bath at temperatures under  $500^{\circ}$ . From this it is inferred that normal weights could be quickly obtained by first heating to a high temperature and then at a lower one, but we have not yet tried the experiment.

A notable increase in weight over a dilute solution of potassium hydroxide is recorded (XXVII., 18). In another similar case, material weighing 0.51882 gram gained in the same way 26 mgms. and subsequently lost 13 mgms. over sulphuric acid. Placed over the alkali again, it gained 23 mgms. and afterwards lost 17 mgms. in the desiccator. In a third instance, on the other hand, material (0.25729 gram) which had been brought within 0.0008 gram of normal weight, gained only 1.6 mgms. over a solution of potassium hydroxide, and more than half of this increase was lost over sulphuric acid. The increase in weight over potassium hydroxide could have

been due only to the absorption of water, and the difference in conduct is perhaps to be explained in the same way as the contradictory behavior of different specimens of material in the air.

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At the time our work was interrupted we were engaged in an endeavor to ascertain how a mixture of known quantities of barium metaborate and carbonate conducts itself when heated to different temperatures, both in the absence and in the presence of carbon dioxide. To prepare the metaborate, equal volumes of equivalent solutions of boric acid and barium hydroxide were mixed, the former being poured into the latter. A precipitate formed, which was dissolved by passing steam into the liquid. A slight cloudiness—supposed to be due to barium carbonate—remained. The solution was filtered, and to portions of the filtrate equal volumes of 95 per cent alcohol were added. The mixture was allowed to stand for three days undisturbed, though at the end of twenty-four hours the precipitate exhibited a distinctly crystalline appearance. After filtering, the material was washed with alcohol, air-dried upon unglazed porcelain plates, and analyzed. It proved to be the metaborate with 5 molecules of water. From a portion of the filtrate, which was not treated with alcohol, wart-like and very compact bunches of crystals separated within a few days, which were found to have the same composition as the material obtained from the alcoholic liquid. Specimens from the two sources gave 28.97 and 28.89 per cent of water, respectively, while the percentage of water in  $\text{BaOB}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  is 28.74. Some of the dehydrated salt which was used in the subsequent experiments gave 68.05 per cent of BaO against 68.7 per cent calculated for  $\text{BaOB}_2\text{O}_3$ .

#### *Experiment XXXI.*

0.97778 gram of the hydrated metaborate, in a platinum boat, was placed in a combustion tube and heated to constant weight in a current of dry air, which had been deprived of its carbon dioxide. The loss in weight was 0.028418 gram = 28.06 per cent. The dehydrated material was next heated in a current, first of dry and then of moist carbon dioxide.

	Weight of material. Gram.	Change in weight. Gram.
1. 2 hours at full red heat in dry $\text{CO}_2$	0.69454	+0.00094
2. " " as in 1	0.69485	+0.00031
3. 2 hours at lower temperature than in 1 and 2	0.69508	+0.00023
4. $1\frac{1}{2}$ " " " " " " 3	0.69500	-0.00008
5. 1 " " " " " " 4	0.69472	-0.00028
6. 2 " " " " in $\text{CO}_2$ saturated with water vapor	0.69540	+0.00068
7. 2 hours as in 6, but at higher temperature	0.69483	-0.00057
8. 2 " at full red heat, $\text{CO}_2$ saturated with water vapor as in 6 and 7	0.69371	-0.00112
9. 2 hours at red heat as in 8	0.69369	-0.00002
10. Stood in the air $28\frac{3}{4}$ hours (5 weighings)	0.69436	+0.00067

The results recorded above indicate that the metaborate of barium is incapable of absorbing carbon dioxide when exposed, at high or low temperatures, in a dry or in a moist atmosphere of that gas; also, that when the salt has been once fully dehydrated, it does not take on an appreciable amount of water in the air. But, as remarked elsewhere, the salt may well conduct itself differently towards carbon dioxide when it is dissolved or suspended in water, as it apparently does towards atmospheric moisture when partially hydrated.

Barium carbonate was next prepared, and the constancy of its weight at high temperature, both in dry and moist carbon dioxide, demonstrated. It was mixed with an equivalent quantity of dehydrated metaborate, and a weighed amount of the mixture was heated in a combustion tube under the conditions specified below. The experiment was a preliminary one and the statements regarding temperature are, of course, very indefinite.

### Experiment XXXII.

Weight of mixture of  $\text{BaOB}_2\text{O}_3 + \text{BaCO}_3 = 1.28219$  gram.

	Weight of material. Grams.	Change in weight. Grams.	Variation from origi- nal weight. Grams.
1. Heated gently 2 hours in a cur- of air free from $\text{CO}_2$	1.28214	-0.00005	-0.00005
2. Heated $2\frac{1}{2}$ hours in a current of air to a temperature at which the glass softened	1.19321	-0.08893	-0.08898



	Weight of material. Grams.	Change in weight. Grams.	Variation from origi- nal weight. Grams.
3. Heated 2 hours as in 2	1.19232	—0.00089	—0.08987
4. Heated at a somewhat lower temperature in current of dry CO <sub>2</sub>	1.19325	+0.00093	—0.08894
5. Stood 1 hour at temperature of room in dry CO <sub>2</sub>	1.19343	+0.00018	—0.08876
6. Warmed the material 1 hour in current of dry CO <sub>2</sub>	1.19869	+0.00526	—0.08350
7. Warmed 1 hour as in 6	1.19965	+0.00096	—0.08254
8. Heated 1 hour, higher than in 6 and 7, but still in dry cur- rent of CO <sub>2</sub>	1.21168	+0.01203	—0.07041
9. Heated 51 hours as in 8 (16 weighings)	1.28097	+0.06929	—0.00122
10. Heated 8 hours as in 8 and 9	1.28134	+0.00037	—0.00085
11. " 35 " to a higher temperature, but still under a red heat, current of CO <sub>2</sub> continued (7 weighings)	1.28333	+0.00199	+0.00114
12. Heated 7 hours to redness in current of dry CO <sub>2</sub>	1.23357	—0.04976	—0.04862
13. Heated 39 hours as in 12 (5 weighings)	1.18647	—0.04710	—0.09572
14. Heated 8 hours to redness in moist CO <sub>2</sub>	1.21508	+0.02861	—0.06711
15. Heated 8 hours as in 14	1.21552	+0.00044	—0.06711
16. " 8 " to redness in air free from CO <sub>2</sub> and H <sub>2</sub> O	1.18599	—0.02953	—0.09620
17. Heated 8 hours to redness in current of moist CO <sub>2</sub>	1.18658	+0.00059	—0.09561
18. Heated 78 hours at varying low temperatures in current of moist CO <sub>2</sub>	1.26457	+0.07799	—0.01762

The experimental work which we have here described is to be regarded as preliminary only. It was undertaken for the purpose of securing sufficient data to enable us to attack advantageously the problem we had in mind. If we had been able to complete our investigation without interruption, or if the circumstances under which it was commenced had been different, doubtless much that we have recorded, having been found unessential, would have been suppressed. The work will be resumed at the earliest opportunity.

## THE COMPOSITION OF NITROGEN IODIDE.

BY F. D. CHATTAWAY

Black explosive compounds formed by the interaction of iodine, or compounds containing iodine, with ammonia have been analyzed from time to time during the past century, but in very few cases do the results agree, those of the same observer, even, often differing widely. It is usually stated that a number of distinct compounds exist, but the statement is based entirely on these discordant results.

Upon close examination most of the analyses prove untrustworthy, for in no case is any evidence brought forward to show that the material analyzed was pure, and in no case are any data given to justify the assumptions made regarding the reactions on which the analyses are based.

Such black explosive substances, both crystalline and amorphous, but resembling each other closely in properties, having been prepared in many ways in a state of undoubted purity, this investigation was undertaken to determine their composition, and to find out whether more than one definite compound could be produced.

Nitrogen iodide so frequently decomposes in more than one way under the influence of reagents that it was a matter of difficulty to find a suitable reaction to employ in its analysis, and to determine the conditions necessary for known products to be formed which admitted of quick and easy estimation. Such a reaction was found, however, in the decomposition of nitrogen iodide by sodium sulphite. In this, if light be excluded, all the nitrogen is obtained as ammonia and all the iodine as hydriodic acid. These can easily be estimated, and the relation between the nitrogen and iodine in any specimen of nitrogen iodide obtained.

This relation is found to be absolutely invariable, 2 molecules of ammonia are always produced to every 3 molecules of hydriodic acid. However the nitrogen iodide is prepared, and whatever its condition, dry or moist, crystalline or amorphous, compact or finely divided, it is the same. This proves that in all reactions which are known to yield nitrogen

iodide only one compound is formed, and that in its molecule 2 atoms of nitrogen are associated with 3 atoms of iodine.

Now, when nitrogen iodide decomposes under the influence of light it breaks up quantitatively into nitrogen and hydriodic acid.<sup>1</sup> Consequently its molecule must contain the same number of atoms of hydrogen as it does atoms of iodine. Since, therefore, in its molecule 2 atoms of nitrogen are associated with 3 atoms of iodine, and these again with 3 atoms of hydrogen, the simplest possible formula for nitrogen iodide is  $N_2H_3I_3$ .

That this formula does represent the composition of nitrogen iodide has been further proved by a large number of analyses of weighed amounts of the pure dry substance prepared in different ways. The percentages of nitrogen and of iodine found agree accurately with those required by this formula.

Further, all attempts to prepare similar bodies of a different composition have completely failed.

It may be taken, therefore, as a definitely proved fact that only one substance of the nature of nitrogen iodide has hitherto been prepared, and that the composition of this is represented by the formula  $N_2H_3I_3$ . The weight of the molecule and the exact manner in which the atoms are linked together still remain to be settled.

#### EXPERIMENTAL PART.

##### *Investigation of the Reaction Employed for Determining the Composition of Nitrogen Iodide.*

When sodium sulphite is slowly added to nitrogen iodide suspended in water until the latter is completely decomposed and the brown color of the liberated iodine just disappears, a colorless acid solution is obtained containing only sodium sulphate, ammonium iodide, and free hydriodic acid. This reaction, one of a very few where nitrogen iodide decomposes in one way only, has been thoroughly investigated in order to base upon it a method of analysis.

The sulphate produced was first shown to be exactly equivalent to the sulphite used. An unknown quantity of nitrogen iodide was titrated with decinormal sodium sulphite and the

<sup>1</sup> See "Action of Light on Nitrogen Iodide", page 159.

resulting sulphate estimated by precipitation with barium chloride.

Two experiments were made: in one 59.3 cc. of decinormal sodium sulphite were used and 0.6914 gram of barium sulphate obtained; in the other 62.5 cc. were used and 0.7288 gram obtained, the weights of barium sulphate equivalent to the quantities of sulphite used being 0.6908 gram and 0.7281 gram, respectively.

The fact was next established that ammonia is the sole compound formed that contains nitrogen. Careful examination showed that neither nitrite, nitrate, hydroxylamine, nor hydrazine was produced.

On distilling with potash, the product obtained by decomposing a large quantity of nitrogen iodide by sodium sulphite an alkaline gas was evolved. This was absorbed by hydrochloric acid and the solution evaporated to dryness. The salt so formed proved to be pure ammonium chloride. On distillation with alkali it gave the theoretical quantity of ammonia, and with platinum chloride it formed ammonium platonic chloride yielding the theoretical weight of platinum on heating.

In two estimations with different specimens of the salt 1.2341 grams and 1.5273 grams yielded 23.1 cc. and 28.5 cc. of decinormal ammonia, theory requiring from ammonium chloride 23.06 cc. and 28.54 cc., respectively.

In three estimations with specimens prepared at different times, 1.8994 grams, 0.7098 gram, 0.8912 gram yielded 0.8361 gram, 0.3109 gram, and 0.3910 gram of platinum, respectively. Percentages of platinum found are 44.01, 43.80, and 43.87; the percentage required for the formula  $2\text{NH}_4\text{Cl} \cdot \text{PtCl}_4$  is 43.9. It has been shown in the preceding paper that the amount of hydriodic acid produced when sodium sulphite reacts with nitrogen iodide is always exactly equivalent to half the amount of sulphite used. Numbers of experiments, which it is not necessary to record, have been made, showing that this result is not affected by the rate at which the sulphite is added or by the consequent appearance or non-appearance of free iodine in the liquid.

The reaction between sodium sulphite and nitrogen iodide

proceeds rapidly and quietly, no bubbles of gas are disengaged if light be excluded, and no other substances besides those mentioned are ever produced. It can, therefore, be used to determine the percentage of nitrogen and of iodine contained in nitrogen iodide.

The ammonia can, of course, be estimated by distilling the product of the action with an excess of caustic potash, but a simpler plan is available. The solution resulting from the action of sodium sulphide upon nitrogen iodide is always found to be acid, since the amount of hydriodic acid produced is greater than that required to neutralize the ammonia simultaneously formed. This excess of acid can easily be estimated by any standard alkali, and since sodium sulphate is neutral and the total amount of hydriodic acid formed is accurately known from the amount of sulphite used, the difference between the amount of hydriodic acid produced and the amount present as free acid represents the amount neutralized by the ammonia formed, and is, consequently, a measure of this. Numbers of experiments have been made to test the accuracy of this method. A quantity of nitrogen iodide was decomposed by a standard solution of sodium sulphite and the free acid present in the resulting solution estimated by a standard solution of baryta. From the amounts of sulphite and of baryta used that of the ammonia formed was calculated. The neutral liquid was then distilled with an excess of caustic potash and the ammonia actually liberated estimated by a standard solution of hydrochloric acid. The results, of which six follow, were in all cases found to be practically identical :

	cc.	cc.	cc.	cc.	cc.	cc.
$\frac{1}{2} \left( \frac{N}{10} \frac{Na_2SO_3}{2} \right) -$						
$\left( \frac{N}{10} \frac{Ba(OH)_2}{2} \right)$	20.5	24.1	32.2	17.6	26.4	29.5
N/10 NH <sub>3</sub> obtained						
by distillation with						
potash	20.4	24.1	32.2	17.6	26.3	29.5

The standard solutions used in the analysis of nitrogen iodide were decinormal solutions of sodium sulphite, hydro-

chloric acid, barium hydroxide, ammonia, and silver nitrate. They were all standardized either directly or indirectly against the silver nitrate.

The strength of the solution of sodium sulphite was determined by titrating with it an unknown quantity of finely powdered iodine, then estimating the amount of free hydriodic acid produced with standard alkali, and finally the total amount of alkaline iodide formed by standard silver nitrate. The purest sodium sulphite available always contains a small amount of uncombined sodium hydroxide, and consequently, when it is converted by iodine into sodium sulphate the amount of hydriodic acid set free is not quite equal to the total amount formed, the difference being neutralized by the alkali present in the sulphite. When preparing the solution of sodium sulphite, therefore, this small amount of free alkali was neutralized by adding the required quantity of sulphurous acid so that when it reacted with pure iodine exactly its own equivalent of hydriodic acid was set free. The actual analysis is best carried out as follows :

A given quantity of pure nitrogen iodide, either moist or dry, generally from 0.5 to 1 gram, is rinsed into a flask with about 25 cc. of distilled water, and the solution of sodium sulphite slowly run in, light being as far as possible excluded until the particles of nitrogen iodide completely disappear and a yellow or brown liquid containing free iodine is formed. The titration is then finished exactly as with iodine, a few drops of starch solution being used as an indicator. A little litmus is then added to this clear liquid, and the free acid neutralized by either baryta or ammonia. The total iodine present is finally estimated by titration with silver nitrate, using a solution of starch rendered deep blue by iodine as an indicator.

The material analyzed has in every case, except where a special note is made, been purified in the same way. Each specimen was washed by decantation with strong ammonia and, where necessary, allowed to stand under it until all soluble foreign matter was removed. It was then filtered off through asbestos at a pump and well washed, first with tenth-normal ammonia and finally three or four times with dis-

tilled water, which ensures the removal of the last traces of adhering ammonia.

Nitrogen iodide, from whatever source, treated in this way does not render blue a neutral solution of litmus when placed in it, nor give any color to chloroform when shaken with it, and finally, as has been shown in the previous section, half the sulphite titre is always equivalent to the silver titre. The latter is the most delicate test of purity that we have. The slightest decomposition caused by washing or by light is at once detected, as is also the presence of any iodide, iodate, or free iodine.

In calculating the results, the amount of hydriodic acid as given by the sulphite titre has been used. The direct estimation by silver nitrate serves as a check on this sulphite titre as well as a proof that no decomposition of the nitrogen iodide used has taken place during washing or under the influence of light. The results are all given in tabular form, each line representing an analysis. In the first column is given the number of cubic centimeters of a decinormal solution of sodium sulphite  $\frac{N}{10} \left( \frac{Na_2SO_3}{2} \right)$  which was found to react with the nitrogen iodide used. The number of cubic centimeters of a decinormal solution of ammonia or other alkali required to neutralize the free hydriodic acid in the resulting solution is given in the second column. The third column contains the number obtained by dividing by 2 the amount of sodium sulphite used; it represents the amount of hydriodic acid produced in the reaction expressed as cubic centimeters of a decinormal solution. In the fourth is stated the number of cubic centimeters of a decinormal solution of silver nitrate which reacted with the hydriodic acid and consequently measures directly the total amount of hydriodic acid formed. The number in this column should agree with that in the third within the limits of experimental error; when this is the case no impurity capable of reacting with either sodium sulphite or silver nitrate can have been present in the nitrogen iodide analyzed, and no decomposition into nitrogen and hydriodic acid can have taken place under the influence of light accidentally admitted during manipulation. The fifth column

contains a number obtained by subtracting the number in the second from that in the third; that is, the amount of free hydriodic acid from the total amount produced. This, therefore, represents the amount of ammonia produced in the reaction.

Now in each analysis

$$\frac{\text{Number in fifth column}}{\text{Number in third column}} = \frac{\text{number of cc. N/10 NH}_3 \text{ produced}}{\text{number of cc. N/10 HI produced}} = \frac{\text{Number of molecules of NH}_3 \text{ formed}}{\text{Number of molecules of HI formed}} = \frac{\text{number of atoms of N in the molecule of nitrogen iodide}}{\text{number of atoms of I in the molecule of nitrogen iodide}}.$$

In the sixth column this ratio as actually obtained in each analysis is given, calculated as a certain number of atoms of nitrogen to 3 atoms of iodine. It is found always to be approximately 2 : 3, the variation from this being in every case within the limits of experimental error.

All known methods of preparing nitrogen iodide have been described in a previous paper,<sup>1</sup> the composition of the substance prepared in every one of these ways has been determined.

To avoid all possibility of error, from twenty to sixty concordant analyses of each product have been made; but to save space the results of a few only are given. In most cases these are successive estimations and consequently the average accuracy reached is shown.

*Analysis of Nitrogen Iodide Prepared by Adding a Solution of Iodine in Potassium Iodide to a Solution of Ammonia.*

The last traces of potassium and ammonium iodide are removed only with difficulty from nitrogen iodide prepared in this way. It is well, therefore, before analysis to allow the product to stand under an excess of 3N-ammonia for a week or so, decanting off and replacing the ammonia solution each day.

<sup>1</sup> "Preparation and Properties of the So-called Nitrogen Iodide": This JOURNAL, 23, 363.



The compound used in analyses 1, 2, and 3 was prepared by adding a decinormal solution of iodine in potassium iodide to a saturated solution of ammonia.

A number of estimations were made to determine whether the concentration of the iodine solution used in the preparation affects the ratio of nitrogen to iodine in the product. The nitrogen iodide used in analyses 4, 5, and 6 was prepared exactly as before except that a normal solution of iodine in potassium iodide was employed.

Number of analyses.	$N \left( \frac{Na_2SO_3}{10} \right)$ cc.	$\frac{N}{10} NH_3$ required to neutralize solution = $\frac{N}{10} HI$ produced in free state = a.	$\frac{1}{2} \left( \frac{N}{10} \frac{Na_2SO_3}{2} \right) =$ cc. b.	$\frac{N}{10} AgNO_3$ required = $\frac{N}{10} HI$ formed.	$\frac{N}{10} NH_3$ formed = cc. b-a.	Ratio between NaI in molecule of nitrogen iodide = $\frac{x}{3} = \frac{b-a}{b}$ .
1	52.4	8.7	26.2	26.2	17.5	2 : 3
2	39.2	6.5	19.6	19.6	13.1	2 : 3
3	77.2	12.9	38.6	38.7	25.7	1.99 : 3
4	40.8	6.8	20.4	20.5	13.6	2 : 3
5	48.0	7.9	24.0	24.0	16.1	2.01 : 3
6	46.6	7.8	23.3	23.3	15.5	1.99 : 3

The concentration of the iodine solution is seen to have no effect whatever upon the composition of the nitrogen iodide. Exactly similar results have been obtained with specimens of nitrogen iodide prepared by the action of solutions of iodine in chloroform and carbon tetrachloride upon ammonia. In both cases the ratio of the number of nitrogen atoms to the number of iodine atoms in the molecule is 2 : 3.

*Analysis of Nitrogen Iodide Prepared by the Action of a Strong Solution of Ammonia upon Solid Iodine.*

The reaction here is much slower than when dissolved iodine is used as the particles become superficially coated with nitrogen iodide which protects them to some extent from further action. To ensure that no iodine remained unattacked the nitrogen iodide thus prepared was allowed to stand for two months under strong (0.880) ammonia, the latter being frequently decanted off and replaced by fresh. The nitrogen iodide used in analyses 1, 2, and 3 was made from finely di-

vided solid iodine, obtained by precipitating a saturated solution of iodine in potassium iodide by excess of water. That used in 4, 5, and 6 was made from very finely powdered iodine.

Number of analyses.	$\frac{N}{10} \left( \frac{Na_2SO_3}{2} \right)$ . cc.	$\frac{N}{10} NH_3$ required to neutralize solution = $\frac{N}{10} HI$ produced in free state. cc.	$\frac{1}{2} \left( \frac{N Na_2SO_3}{10} \right) = \frac{N}{10} HI$ formed. cc.	$\frac{N}{10} AgNO_3$ required = $\frac{N}{10} HI$ formed. cc.	$\frac{N}{10} NH_3$ formed. cc.	Ratio between N and I in molecule of nitrogen iodide.
1	47.0	7.8	23.5	23.6	15.7	2 : 3
2	52.1	8.9	26.05	26.0	17.35	1.99 : 3
3	38.2	6.5	19.1	19.2	12.6	1.97 : 3
4	39.9	6.8	19.95	20.0	13.15	1.97 : 3
5	29.4	5.0	14.7	14.8	9.7	1.98 : 3
6	35.2	5.9	17.6	17.7	11.7	1.99 : 3

*Analysis of Nitrogen Iodide Prepared by the Action of an Alcoholic Solution of Iodine upon Ammonia.*

Experiments were next made with the nitrogen iodide which is obtained, mixed with more or less iodoform, whenever iodine dissolved in alcohol is allowed to act upon ammonia dissolved either in water or alcohol. The analysis of the nitrogen iodide contained in this mixture, if it be washed free from alcohol and soluble impurities, can be carried out as though the iodoform were not present, for this is not appreciably attacked during the titrations. The material used in analyses 1, 2, and 3 was prepared by adding a saturated alcoholic solution of iodine to strong aqueous ammonia. It smelled strongly of iodoform, and yellow crystals of this compound were seen floating in the colorless liquid obtained after titration with sodium sulphite. Analyses 4, 5, and 6 were performed with nitrogen iodide obtained by adding a cooled saturated solution of iodine in absolute alcohol to cooled anhydrous alcohol saturated with dry ammonia. It was very carefully washed, using a filter-pump, first with alcoholic ammonia, then with cool alcohol, and finally rapidly with water.

Number of analyses.	$\frac{N}{10} \left( \frac{Na_2SO_3}{2} \right)$ cc.	$\frac{N}{10}$ $NH_3$ required to neutralize solution = $\frac{N}{10}$ HI produced in free state.	$\frac{1}{2} \left( \frac{N}{10} \frac{Na_2SO_3}{2} \right)$ cc. = $\frac{N}{10}$ HI formed.	$\frac{N}{10}$ $AgNO_3$ required = $\frac{N}{10}$ HI formed.	$\frac{N}{10}$ $NH_3$ formed.	Ratio between N and I in molecule of nitrogen iodide.
1	51.3	10.3	30.65	30.7	20.35	1.99 : 3
2	51.3	8.8	25.65	25.6	16.95	1.98 : 3
3	46.4	8.0	23.2	23.3	15.2	1.96 : 3
4	63.3	10.5	31.65	31.7	21.15	2 : 3
5	40.0	6.7	20.0	20.1	13.3	1.99 : 3
6	29.6	4.9	14.8	14.9	9.9	2 : 3

It is seen that the ratio of nitrogen to iodine in nitrogen iodide produced in this way, although it is never obtained quite free from foreign matter, is the same as in nitrogen iodide prepared by other methods.

*Analysis of Nitrogen Iodide Prepared by Adding Ammonia to a Solution of Potassium Hypiodite Containing an Excess of Potash.*

Either amorphous or crystalline nitrogen can be produced at will by this reaction according to the concentration of the potassium hypiodite in the solution used. When the concentration of the hypiodite is above a certain limit the compound is formed so rapidly that it cannot assume the crystalline form.

Analyses 1, 2, and 3 were made using amorphous nitrogen iodide prepared thus.

When the concentration of the hypiodite is above the limit at which nitrogen iodide is first produced and below the limit at which it separates in an amorphous state, it assumes a crystalline form, the size and perfection of the crystals being greater the slower the rate of deposition.

Analyses 4, 5, and 6 were made with finely crystallized nitrogen iodide obtained in this way.

Number of analyses,	$\frac{N}{10} \left( \frac{Na_2SO_3}{2} \right)$ , cc.	$\frac{N}{10}$ $NH_3$ required to neutralize solution = $\frac{N}{10}$ HI produced in free state, cc.	$\frac{1}{2} \left( \frac{N}{10} \frac{Na_2SO_3}{2} \right)$ $N$ $\frac{HI}{10}$ formed, cc.	$\frac{N}{10}$ $AgNO_3$ required = $\frac{N}{10}$ HI formed, cc.	$\frac{N}{10}$ $NH_3$ formed, cc.	Ratio between N and I in molecule of nitrogen iodide.
1	43.8	7.3	21.9	21.9	14.6	2 : 3
2	39.5	6.6	19.75	19.8	13.15	1.99 : 3
3	48.9	8.1	24.45	24.5	16.35	2 : 3
4	55.9	9.3	27.95	28.0	18.65	2 : 3
5	63.6	10.6	31.8	31.8	21.2	2 : 3
6	94.6	15.8	47.3	47.3	31.5	1.99 : 3

The relation between the nitrogen and iodine in the substance obtained by this method is seen to be the same whether it is amorphous or crystalline, and to be identical with the relation invariably found.

*Analysis of Nitrogen Iodide Prepared by the Action of Iodine Monochloride on Ammonia and of Nitrogen Iodide Obtained by the Interaction of Calcium Hypochlorite and Ammonium Iodide.*

A precisely similar result was obtained in analyses 1, 2, and 3 of the following table, in which amorphous nitrogen iodide obtained by adding a decinormal solution of iodine monochloride in dilute hydrochloric acid to a 3N-solution of ammonia was employed.

Analyses 4, 5, and 6 were made with crystalline nitrogen iodide obtained by dissolving the above in hot ammonia solution and cooling the liquid. This apparent recrystallization must be very rapidly performed and consequently only a very small amount of nitrogen iodide can be obtained thus at a time. If too long a period be taken either in heating the solution or in cooling it, much ammonium iodate is produced but little or no crystalline nitrogen iodide.

It is seen that the relation between the nitrogen and iodine in the compound is not affected by this apparent recrystallization.

The nitrogen iodide used in analyses 7, 8, and 9 was made by adding an excess of a clear solution of bleaching-powder

to a solution of ammonium iodide. Nitrogen iodide is precipitated mixed with a variable amount of calcium iodate, the last traces of which are difficult to remove. The material analyzed was freed from this substance by thoroughly washing with decinormal ammonia. The relation of nitrogen to iodine was found to be the same as in nitrogen iodide prepared in any other way.

Number of analyses.	$\frac{N}{10} \left( \frac{Na_2SO_3}{2} \right)$ cc.	$\frac{N}{10} NH_3$ required to neutralize solution = $\frac{N}{10} HI$ produced in free state.	$\frac{1}{2} \left( \frac{N}{10} \frac{Na_2SO_3}{2} \right) = \frac{N}{10} HI$ formed.	$\frac{N}{10} AgNO_3$ required = $\frac{N}{10} HI$ formed.	$\frac{N}{10} NH_3$ formed.	Ratio between N and I in molecule of nitrogen iodide.
1	171.2	28.5	85.6	85.5	57.1	2 : 3
2	128.4	21.4	64.2	64.2	42.8	2 : 3
3	165.5	27.6	82.75	82.8	55.15	1.99 : 3
4	61.5	10.3	30.75	30.7	20.45	1.99 : 3
5	66.9	11.1	33.45	33.5	22.35	2 : 3
6	80.2	13.4	40.1	40.2	26.7	1.99 : 3
7	36.2	6.0	18.1	18.2	12.1	2 : 3
8	39.2	6.6	19.6	19.8	13.0	1.98 : 3
9	30.4	5.1	15.2	15.3	10.1	1.99 : 3

*Composition of the So-called "Nitrogen Iodide."*

All the preceding results show that the relation by weight between the nitrogen and iodine in the various specimens of nitrogen iodide analyzed does not vary either with the mode of preparation or the state of aggregation of the compound, and that this relation is 2 : 3 when expressed in terms of the atomic weights of the two elements.

The reactions in which the compound is formed are, moreover, essentially the same. They all lead to the production of ammonium hypoiodite, from which it is produced by a reversible change. We have, therefore, every ground for concluding that only one such compound exists, and that in its molecule 2 atoms of nitrogen are associated with 3 atoms of iodine.

Now it is shown in the following paper that when nitrogen iodide is exposed to sunlight it breaks up quantitatively into nitrogen and hydriodic acid. This proves that the molecule

of the compound contains only nitrogen, hydrogen, and iodine atoms and that each atom of iodine is associated with 1 atom of hydrogen. Therefore, since the foregoing analyses have shown that in nitrogen iodide 2 nitrogen atoms are associated with 3 iodine atoms and, since the decomposition by light shows that these latter are associated with 3 hydrogen atoms, the simplest formula which expresses its composition is  $N_2H_3I_3$ . The correctness of this conclusion has been confirmed by the analysis of weighed quantities of the dry compound.

*Analysis of Weighed Quantities of Nitrogen Iodide.*

Nitrogen iodide so readily undergoes decomposition that it is somewhat difficult to obtain it free from moisture in a state of purity. It can, however, be dried without change over lime or baryta in an atmosphere of ammonia if light be entirely excluded. A number of analyses of weighed amounts of nitrogen iodide have consequently been made.

The following procedure was adopted: Nitrogen iodide was thoroughly washed with strong ammonia and allowed to drain. From 0.5 to 1 gram of this moist material was then spread in a thin layer on a weighed watch-glass and exposed for several days in an atmosphere of pure ammonia over baryta till its weight was constant. It was then placed for a very short time over sulphuric acid in a vacuum to remove traces of ammonia gas, and finally was weighed, detached from the watch-glass after moistening with water, and analyzed as previously described. The operations were conducted in a cool cellar and light, except that from a small gas flame during transference and weighing, was entirely excluded. The nitrogen iodide must be placed very loosely on the watch-glass; if it be pressed into a compact mass before drying it almost always explodes during titration with the sulphite. This is dangerous, as the explosion of not more than 0.01 part of a gram suspended in water is sufficient to shatter a stout flask.

A considerable number of such analyses of dry nitrogen iodide prepared in different ways have been made. The ratio between the ammonia and hydriodic acid produced is exactly the same as when the moist substance is employed and the percentages of nitrogen and iodine agree with those required by

the formula  $N_7H_3I_3$ , which may thus be considered as definitely established.

The results are recorded exactly as before, except that in the first column the weight of dry nitrogen iodide used is given, while in two additional columns, 8 and 9, the percentages of nitrogen and iodine, respectively, are given.

Analyses 1, 2, and 3 were made with nitrogen iodide prepared by the action of a strong solution of ammonia on pure precipitated iodine. Those numbered 4, 5, and 6 with finely crystalline nitrogen iodide obtained by adding ammonia to a solution of potassium hypoiodite, while that used in 7 and 8 was made by taking amorphous nitrogen iodide prepared from iodine monochloride and recrystallizing it by heating it with strong ammonia and rapidly cooling the solution.

The formula  $N_7H_3I_3$  requires 92.44 per cent of iodine, 6.82 per cent of nitrogen, and 0.73 per cent of hydrogen ( $I = 126.85$ ,  $N = 14.04$ ,  $H = 1.01$ ).

Number of analysis.	Weight of nitrogen iodide used.	$N \left( \frac{Na_2SO_3}{2} \right)$	$\frac{N}{10} NH_3$ required to neutralize solution = $\frac{N}{10} HI$ produced in free state.	$\frac{N}{10} \left( \frac{Na_2SO_3}{2} \right) = \frac{N}{10} HI$ formed.	$\frac{N}{10} AgNO_3$ required = $\frac{N}{10} HI$ formed.	$\frac{N}{10} NH_3$ formed.	Ratio between N and I in molecule of nitrogen iodide.	Percentage of iodine obtained.	Percentage of nitrogen obtained.
	Gram.	cc.	cc.	cc.	cc.	cc.			
1	0.5937	86.5	14.5	43.25	43.3	28.75	1.99 : 3	92.41	6.80
2	0.2733	39.8	6.7	19.9	19.9	13.2	1.99 : 3	92.36	6.78
3	0.3794	55.4	9.2	27.7	27.7	18.5	2 : 3	92.61	6.85
4	0.3758	54.8	9.1	27.4	27.4	18.3	2 : 3	92.49	6.84
5	0.3774	55.0	9.2	27.5	27.4	18.3	1.99 : 3	92.43	6.81
6	0.3378	49.2	8.2	24.6	24.7	16.4	2 : 3	92.38	6.82
7	0.4156	60.5	10.1	30.25	30.3	20.15	1.99 : 3	92.33	6.81
8	0.3075	44.8	7.5	22.4	22.4	14.9	1.99 : 3	92.40	6.80

*Experiments made to Determine whether Similar Substances of Composition Differing from  $N_7H_3I_3$  Could Be Produced.*

The preceding investigation has shown that in all reactions which yield nitrogen iodide the substance produced is a single definite compound, the composition of which is represented by the formula  $N_7H_3I_3$ . The results of previous ob-

servers have, however, differed so widely that it seemed conceivable that other substances might be produced in the reactions, although, under the conditions employed, these had never been obtained. Consequently, experiments were made to determine whether any other substance could be produced, but in every case with a negative result. A number of analyses, which it is not necessary to record, were first made to determine whether the compound had the same composition at the instant of its formation as after standing for a considerable time under ammonia. It was found that the ratio of nitrogen to iodine in the compound is exactly the same at the moment of its formation as after standing for months under strong ammonia.

A number of experiments have been made to decide whether nitrogen iodide can combine, however loosely, with ammonia as it is conceivable, though improbable, that such an unstable compound might be decomposed by the water used to remove the last traces of adhering ammonia. Nitrogen iodide prepared by adding a decinormal solution of iodine in potassium iodide to ammonia, after thoroughly washing, was allowed to stand for two months under 0.880 ammonia; it was then filtered off, well washed with strong ammonia, and finally twice with decinormal ammonia; the mass was then pressed dry between filter-paper, and small pieces from the middle taken for analysis.

Experiments 1, 2, and 3 in the following table give the results. The ratio between nitrogen and iodine is practically the same as before, the nitrogen being very slightly too high owing to traces of ammonia adhering to the damp mass.

Further experiments were made with the same object, a slightly different method being adopted. Amorphous nitrogen iodide, after standing under 0.880 ammonia for two months, was thoroughly washed with strong ammonia, and the pulp thus obtained mixed with distilled water. After subsidence, 25 cc. of the lower layer containing suspended nitrogen iodide was removed and titrated as usual. Some of the supernatant liquid was then filtered off and the ammonia per cubic centimeter estimated.

Assuming that amorphous nitrogen iodide has the same



specific gravity as crystalline, the volume occupied by it can be calculated from the sulphite titre and, deducting this from the 25 cc. of liquid taken, we obtain the volume of the ammonia solution in which it was suspended, we also know how much ammonia this contains. Subtracting the amount from the total quantity found in the estimation, that yielded by the nitrogen iodide is obtained. We thus find the relation between the ammonia and hydriodic acid, yielded by nitrogen iodide which has never been removed from a solution of ammonia. This is found to be precisely the same as in the washed specimens.

The ammonia solution in which the nitrogen iodide was finally suspended was always diluted to such a point that the product of the titration with sulphite was slightly acid. For clearness the details are stated as in previous tables, the amount of ammonia present in the solution suspending the nitrogen iodide being added to that required to neutralize the liquid obtained after titration with sodium sulphite.

The results given in experiments 4, 5, and 6 show conclusively that the molecule of nitrogen iodide is unable to combine with ammonia in aqueous solution.

Number of analyses.	$\frac{N}{10} \left( \frac{Na_2SO_3}{2} \right)$ , cc.	$\frac{N}{10}$ $NH_3$ required to neutralize solution = $\frac{N}{10}$ HI produced in free state.	$\frac{1}{2} \left( \frac{N}{10} \frac{Na_2SO_3}{2} \right)$ $\frac{N}{10}$ HI formed.	$\frac{N}{10}$ $AgNO_3$ required = $\frac{N}{10}$ HI formed.	$\frac{N}{10}$ $NH_3$ formed.	Ratio between N and I in molecule of nitrogen iodide.
1	97.8	16.2	48.9	48.9	32.7	2.006 : 3
2	97.0	16.1	48.5	48.6	32.4	2.004 : 3
3	85.1	14.1	42.55	42.5	28.45	2.005 : 3
4	83.8	14.0	41.9	42.0	27.9	1.99 : 3
5	97.8	16.3	48.9	48.9	32.6	2 : 3
6	69.0	11.7	34.5	34.4	22.8	1.98 : 3

The methods of preparing nitrogen iodide and the actions which result when it is treated with potash or ammonia prove that the hypiodites have no action upon the compound.

Experiments have also been made which show that iodine itself is neither able to combine with the substance nor to replace the hydrogen atoms contained in the molecule.

When nitrogen iodide is digested for some hours with a solution of iodine, it apparently suffers no change but, on filtering off and washing, a little iodine is found to be retained, apparently deposited upon the solid particles. That no combination has taken place is proved by the fact that a very small and variable quantity only is thus attached, and by the fact that it can be recognized as iodine by its smell and by shaking with chloroform. The amount of this retained iodine can be estimated by taking advantage of two circumstances : first, that all the iodine present as nitrogen iodide oxidizes double the amount of sodium sulphite that it would were it present as the free element, while any iodine present as such simply oxidizes its equivalent ; and second that silver nitrate estimates the total amount of hydriodic acid produced, and gives the same result whether the iodine originally replaced hydrogen or was present in the free state.

If  $a$  be the number of cubic centimeters of decinormal sodium sulphite which reacts with a given quantity of such a mixture of free iodine and of nitrogen iodide, either with its hydrogen replaced by iodine or not, and if  $b$  represent the number of cubic centimeters of decinormal silver nitrate required to react with the hydriodic acid produced, then if  $x$  be the amount of iodine present as nitrogen iodide, and if  $y$  be the amount present in the free state measured in cubic centimeters of a decinormal solution, we have :

$$a = 2x + y, \qquad b = x + y,$$

whence we have

$$x = a - b \qquad \text{and} \qquad y = 2b - a.$$

The experiments were carried out as follows : Nitrogen iodide was shaken up with an excess of a decinormal solution of iodine in potassium iodide and left for six hours, all light being excluded. At the end of that time the substance was filtered off, washed with water, and titrated as usual.

In the reaction of the product with the sodium sulphite all the ammonia liberated must come from the nitrogen iodide and, since the amount of free hydriodic acid is known from the alkali titre, and the total amount of hydriodic acid pro-

duced from the silver nitrate titre, the difference between the two, as before, gives the amount.

We know, therefore, the amount of nitrogen and can calculate  $x$ , that is the amount of iodine associated with it. We thus obtain the relation between the nitrogen and the iodine contained in the product, and this is found to be approximately 2 : 3, exactly as before treatment with the iodine. This proves that iodine has no substituting or other action on nitrogen iodide. Very large amounts were titrated each time to ensure accuracy. Experiments 1, 2, and 3 were made with amorphous nitrogen iodide prepared by digesting finely divided precipitated iodine for two months with strong ammonia, while in 4, 5 and 6 crystalline nitrogen iodide was used.

Number of analysis.	$\frac{N}{10} \frac{N\frac{1}{2}SO_3}{2} = a.$ cc.	$\frac{N}{10} \frac{NH_3 \text{ required to neutralize solution}}{10} - \frac{N}{10} \frac{HI \text{ produced in free state.}}{10}$ cc.	$\frac{N}{10} \frac{AgNO_3 \text{ required HI formed} = b.}{10}$ cc.	$\frac{N}{10} \frac{NH_3 \text{ formed.}}{10}$ cc.	$x = \frac{N}{10} \frac{\text{iodine present as nitrogen iodide.}}{10}$ cc.	$y = \frac{N}{10} \frac{\text{iodine present as free element.}}{10}$ cc.	Percentage of total iodine present as free element. cc.	Ratio between N and I in nitrogen iodide after treatment with iodine.
1	210.5	37.9	106.8	68.5	103.7	3.1	2.9	1.98 : 3
2	227.4	40.4	115.3	74.9	112.1	3.2	2.77	2 : 3
3	250.1	45.6	126.9	81.6	123.2	3.7	2.91	1.98 : 3
4	230.1	42.0	117.1	75.1	113.0	4.1	3.50	1.99 : 3
5	192.4	35.1	97.8	62.7	94.6	3.2	3.27	1.98 : 3
6	381.9	69.7	194.3	124.6	187.6	6.7	3.44	1.99 : 3

### Discussion of Previously Published Analyses.

In the preceding pages it is shown that the same substance is formed in all reactions which are known to yield nitrogen iodide, and that this is a definite compound whose composition is represented by the formula  $N_2H_3I_3$ . The statement that a number of distinct substances can be produced in these reactions, although so generally accepted, is thus shown to be inaccurate. The analytical results upon which alone this statement is based must, therefore, be faulty or the substances analyzed must have been impure or partially decomposed by the treatment preceding or during analysis.

These analyses have been made with unknown weights of material, and consequently only the ratio between the contained iodine and nitrogen determined, the formulæ being deduced from this on the assumption, which we elsewhere show to be erroneous, that nitrogen iodide is formed from ammonia by substitution.

Bineau, in 1845, first attempted to analyze the substance, making three estimations of the amounts of ammonium iodide and hydriodic acid produced when it is decomposed by hydrogen sulphide.

Gladstone, seven years later, published two analyses, using Bineau's method in one and the decomposition of the compound by sulphurous acid in the other. His results are similar to Bineau's, the ratio obtained being roughly 1 : 2. Bunsen, in the same year, published two analyses, using the decomposition by hydrogen chloride. He obtained the ratios N : I (2.04 : 3) and (4 : 11.9) in specimens prepared differently. These numbers of Bunsen, which did not agree at all with his own, caused Gladstone, still employing sulphurous acid, to publish four more analyses which, although differing among themselves by nearly 9 per cent, roughly confirmed his previous estimations. Stahlschmidt, ten years later, in seven analyses obtained ratios of nitrogen to iodine varying according to the mode of preparation from 1 : 1.21 to 1 : 2.98. Mallet, in 1879, then published some analyses of nitrogen iodide which, in most cases, he washed with alcohol, a liquid which very rapidly decomposes it. He obtained varying ratios, such as 1 : 2.94, 1 : 2.47, and 1 : 2.13. Raschig, in 1885, in consequence of the very contradictory results hitherto obtained, endeavored, but unsuccessfully, to prepare pure substances corresponding to the formulæ hitherto suggested ; he obtained discrepant results and states at the end of his paper that the question of the composition must still be regarded as an open one. Since then Szuhay published some numbers, in 1893, but they may be disregarded, as he prefaces his work by the statement that he has convinced himself that by the action of iodine on ammonia no other substances besides nitrogen iodide and ammonium iodide are produced.

On considering the work of all these chemists, several

things appear noteworthy. In the few cases where more than one analysis of the same material is published the results differ far more than can be accounted for by experimental error, while substances of very different compositions are obtained by reactions essentially the same.

The methods of analysis, again, which have been employed cannot have given accurate results for, as we show in other papers, when hydrogen sulphide, sulphurous acid, or hydrochloric acid acts upon nitrogen iodide, the whole of the nitrogen is not obtained as ammonia but a considerable and variable amount is liberated as gas. Further, no precaution, apparently, has ever been taken to exclude light during the operations.

These facts would account for many discrepancies and a further source of error is found in the readiness with which the compound is decomposed if washed too long before analysis.<sup>1</sup> Several years ago, on first taking up its study, specimens of nitrogen iodide prepared in various ways were analyzed, the material being washed, as recommended by previous observers, till the alkaline reaction of the filtrate disappeared or was marked by the liberation of iodine. The numbers obtained were not sufficiently concordant to justify their publication, but they gave a ratio between the nitrogen and iodine atoms approximately 1 : 2. A very large number of analyses were afterwards made to see if close agreement between the results could not be obtained, and the present research is the outcome. It was first found that neither sodium thiosulphate, hydrogen sulphide, nor hydrochloric acid could be used in the analyses,—the thiosulphate because irregular oxidation was liable to take place, and hydrogen sulphide and hydrochloric acid because they always caused the liberation of a small and variable amount of nitrogen.

It was next discovered that even diffused light must be excluded during the operations,<sup>2</sup> and finally, that any prolonged washing with water causes a very noticeable decomposition. To obtain accurate results it is necessary before analysis to

<sup>1</sup> Compare "Action of Reducing Agents upon Nitrogen Iodide," this JOURNAL, 23, 369.

<sup>2</sup> *Ibid.*

wash the compound thoroughly with decinormal ammonia, and finally to remove any traces of this adhering to the solid by rapidly washing three or four times with pure water. In the material so treated neither ammonia nor iodine is present and the amount of any reducing agent oxidized by it is exactly double the quantity equivalent to the iodine it contains. If the washing be continued beyond this point, the filtrate becomes slightly alkaline and colored yellow by iodine, iodine can be recognized in the solid mass, and the amount of any reducing agent oxidized is less than double the amount equivalent to the contained iodine.

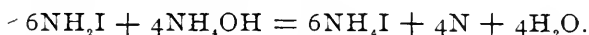
It is very probable that the three causes, unsuitable reaction, decomposition by light during manipulation, and decomposition by prolonged washing, adequately account for the varying results, because in every analysis yet recorded, except a single one of Bunsen's, less than 2 atoms of nitrogen have been found associated with 3 atoms of iodine, as would be the case if any or all of these causes were operative. Since single analyses only have, as a rule, been made of specimens prepared in different ways, chemists have concluded that they had in their hands distinct, but similar, substances of definite composition. Mixtures of any composition from nitrogen iodide,  $N_2H_4I_3$ , to pure iodine can, in fact, be obtained by washing nitrogen iodide continuously. To show this, about a kilogram of nitrogen iodide was taken, placed in a funnel closed by a plug of asbestos, and a slow stream of distilled water allowed to percolate through the mass; every few hours a portion was removed, rapidly washed by water, and analyzed. The amount of nitrogen associated with a given weight of iodine was found gradually, but absolutely continuously, to become less and less until at the end of several weeks only a small quantity of pure iodine remained. Obviously, if only a few analyses were made, mixtures of any possible composition containing less nitrogen than  $N_2H_4I_3$  might be obtained and might be assumed, in the absence of evidence to the contrary, to be definite substances.

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## THE ACTION OF LIGHT ON NITROGEN IODIDE.

BY F. D. CHATTAWAY AND K. J. P. ORTON.

Guyard, who first studied the decomposition of nitrogen iodide by light in the presence of water and ammonia, found that diffused light caused a slow evolution of nitrogen, while direct sunlight brought about a rapid effervescence. On account of its extreme sensitiveness he suggested forms of photometers in which nitrogen iodide was employed. He states that the products of the decomposition are nitrogen, ammonium iodide, and traces of ammonium iodate, and writes the following equation to express the reaction :



Though the results are nowhere given, he remarks that his actual experimental numbers agree rather with the atomic ratio (10 : 7) for iodine to nitrogen than with the ratio (3 : 2) required by the above equation. He does not say whether, in obtaining this ratio (10 : 7), he considers only the iodine present as iodide or the total iodine as iodide and iodate, in fact he has left no record of any estimation of iodate.

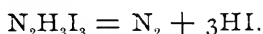
Guyard also describes the action of light on iodine suspended in ammonia solution and mentions that from 1.27 grams of iodine 33.5 cc. of nitrogen were evolved. This is the only instance in which he gives numerical data.

Having obtained nitrogen iodide of a definite and known composition we have investigated the action of light upon it. When nitrogen iodide suspended in a solution of ammonia is exposed to light, nitrogen is evolved and the solid disappears, while ammonium iodide and ammonium iodate are formed in the liquid. The quantity of the latter is never negligible, although it varies within wide limits. It is, moreover, formed from ammonium hypoiodite, which is the first product of the action, and can always be recognized in the solution during the decomposition.

These substances are formed in two reactions which go on simultaneously, one, a simple decomposition caused by light, the other, an action which goes on equally well in the dark,

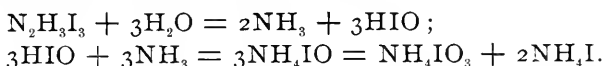
due to the ammonia solution in which the nitrogen iodide is suspended.

The main reaction is the simple one. Under the influence of light the nitrogen iodide breaks down quantitatively into nitrogen and hydriodic acid, thus :



The ammonia present apparently only affects this action by combining with the hydriodic acid formed, and so preventing further secondary reactions.

While this decomposition is taking place a variable amount of the nitrogen iodide is hydrolyzed, the ammonium hypiodite so formed being slowly transformed into ammonium iodide and ammonium iodate, thus :



The amount of hydrolysis varies with the temperature and the length of time required for the decomposition. Usually, on a bright, sunny day, from 2-4 per cent only is hydrolyzed while as high a percentage as 25 has been observed when the day has been dull and the decomposition consequently very slow.<sup>1</sup>

The action of light on iodine suspended in ammonia is really an action on nitrogen iodide itself. We prove later that in the interaction of iodine and ammonia half the iodine becomes ammonium iodide and half ammonium hypiodite, which for the most part decomposes into nitrogen iodide. The latter then reacts exactly as when it is previously prepared and suspended in ammonia.

Similar actions take place if the nitrogen iodide is suspended in water ; but in this case a further complication is introduced by the action of the hydriodic acid produced on the still undecomposed nitrogen iodide,<sup>2</sup> a fact entirely overlooked by Guyard.

<sup>1</sup> Guyard says that he found the atomic ratio of iodine to nitrogen 10 : 7. In certain of our experiments the total iodine (as iodide and iodate) present, after the decomposition was complete, bore to the nitrogen evolved the ratio 10 : 7. Such is the case when 4 per cent of the nitrogen iodide has been hydrolyzed. Obviously, therefore, Guyard did not estimate the iodate separated, and consequently missed its significance.

<sup>2</sup> In an article to be published later it will be shown that nitrogen iodide and hydriodic acid react thus :  $\text{N}_2\text{H}_3\text{I}_3 + 5\text{HI} = 2\text{NH}_4\text{I} + 3\text{I}$ .



Dry nitrogen iodide also is rapidly decomposed by light, nitrogen being evolved while free iodine and ammonium iodide are formed. Here also the first action, without doubt, is the simple decomposition into nitrogen and hydriodic acid; the latter then reacts with the still undecomposed solid, forming iodine and ammonium iodide.<sup>1</sup>

The explosive decomposition of nitrogen iodide caused by heat or percussion is probably also a sudden resolution into nitrogen and hydriodic acid similar to the slow decomposition caused by light. The iodine liberated may be formed either by decomposition of the hydriodic acid at the high temperature of the explosion or by its action on a portion of the original material. If such an explosion be closely watched, a white fume of hydrogen iodide can always be seen surrounding the mass of violet iodine vapors formed.

#### EXPERIMENTAL PART.

A preliminary experiment was made to determine the substances formed in the decomposition of nitrogen iodide by light. About 2 grams of the pure iodide were shaken up with 200 cc. of 5N-ammonia solution and exposed to diffused light in a flask arranged so that the gas evolved could be collected. Throughout the decomposition nothing but nitrogen was given off. The supernatant liquor became of a very faint yellow color. Fifty cc. were removed, filtered through asbestos, and titrated with standard sodium arsenite, which is oxidized by hypiodite but not by iodate.<sup>1</sup> One cc. of tenth-normal arsenite was oxidized. When the whole of the iodide had disappeared the ammonia was boiled off, after adding caustic potash, and the iodate and iodide estimated. On acidifying with dilute sulphuric acid, the iodine which was set free was titrated with standard sodium sulphite. Then the total iodine (now all present as hydriodic acid) was estimated by a tenth-normal solution of silver nitrate. 21.1 cc. of tenth-normal sodium sulphite and 112.2 cc. tenth-normal silver nitrate were required. Now one-sixth of the sulphite titre represents iodine as iodate, and three times the iodine as iodate equals the total

<sup>1</sup> Lonnes (*Ztschr. anal. Chem.*, **33**, 409), in a valuable and exhaustive paper on the titration of iodine by solutions of arsenite, has shown that the latter is oxidized by hypiodite and not by iodate.

iodine (as iodide and iodate) formed by hydrolysis of nitrogen iodide (see equations given above). Therefore 10.55 cc. of a tenth-normal solution of iodine (*i. e.* one-half the sulphite titre) represents the amount of iodine in the nitrogen iodide which has been hydrolyzed, while 112.2 cc. represent the total amount of iodine in the nitrogen iodide used. The percentage of nitrogen iodide hydrolyzed is  $\frac{10.55 \times 100}{112.2} = 9.4$ . No other substances besides nitrogen, ammonium iodide, hypoiodite, and iodate were formed.

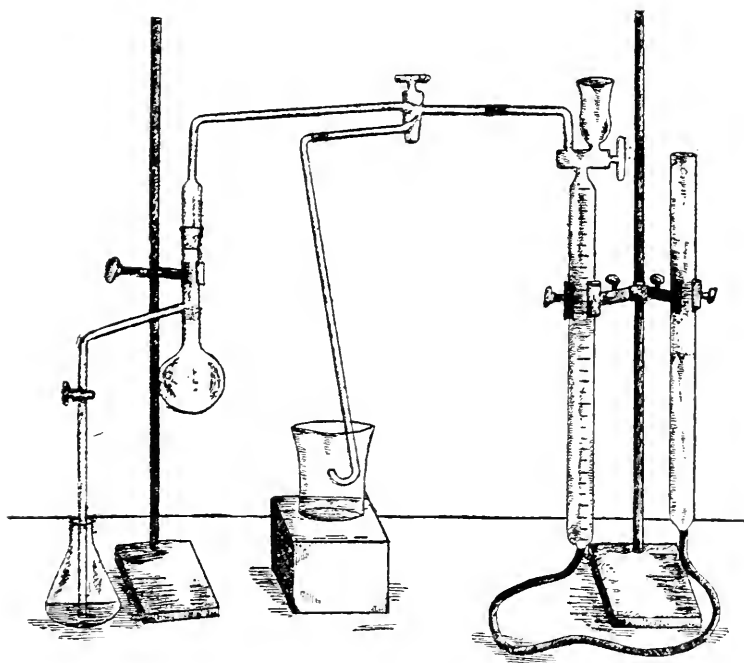
*Estimation of Each Substance Produced when Nitrogen Iodide, Suspended in a Solution of Ammonia, Decomposes under the Influence of Light.*

It is obvious from the above experiment that the hydrolysis which accompanies the decomposition by light cannot be neglected. In the following experiments each product was estimated; *viz.*, nitrogen, ammonium iodide, and ammonium iodate. The decomposition was effected in the apparatus shown in the illustration.

A round-bottomed flask of 150 cc. capacity was ground on to a tube sealed to one limb of a three-way tap. This tap was connected by its second limb with a Lunge's nitrometer, and by its third to a delivery tube by which the nitrogen collected in the nitrometer could be transferred to a graduated tube standing over water, and measured.

In the experiments, crystalline nitrogen iodide was thoroughly washed and placed in the flask under a solution of 3N-ammonia. Air was displaced from the apparatus by drawing in more ammonia solution by the side-tube. It was found necessary to place a plug of asbestos in the tube just above the neck of the flask to prevent small particles of nitrogen iodide attached to bubbles of nitrogen being carried over into the nitrometer during the evolution of gas.

As soon as the air was displaced the flask was exposed to bright sunlight, which was also reflected on to the nitrogen iodide by a large concave mirror. Under these conditions two hours were generally sufficient for complete decomposition.



When all the nitrogen iodide had disappeared the nitrogen was driven over into the measuring tube and its volume determined, while the liquid in which it had decomposed and the washings of the connecting tube were collected and analyzed as described above. The total iodine (*i. e.* the silver nitrate titre) less the iodine, as iodide and iodate formed by hydrolysis (*i. e.* half the sulphite titre), measures the amount of hydriodic acid formed in the decomposition of nitrogen iodide into nitrogen and hydriodic acid. The results of five experiments are given in the following table. In the fourth column are numbers obtained by subtracting those in the second from those in the third. They give as cubic centimeters of a tenth-normal solution the amount of hydriodic acid formed from the nitrogen iodide, which has been decomposed into nitrogen and hydriodic acid. In the fifth column is given the number of cubic centimeters of nitrogen at normal temperature and pressure calculated from this hydriodic acid

which should be obtained, supposing that the nitrogen iodide breaks up according to the equation



In the sixth column is given the number of cubic centimeters of nitrogen actually measured.

(The mass of 1 cc. of nitrogen at 0° and 760 mm. is taken as 0.00125 gram.)

$\frac{\text{N}}{10} \frac{\text{Na}_2\text{SO}_3}{2}$ cc.	$\frac{1}{2} \left\{ \frac{\text{N}}{10} \frac{\text{Na}_2\text{SO}_3}{2} \right\} = \frac{\text{N}}{10} \text{I}$ in nitrogen iodide hydrolyzed.	$\frac{\text{N}}{10} \text{AgNO}_3 = \frac{\text{N}}{10} \text{I}$ in total amount of nitrogen iodide used in ex- periment.	$\frac{\text{N}}{10} \text{AgNO}_3 - \frac{1}{2} \left\{ \frac{\text{N}}{10} \frac{\text{Na}_2\text{SO}_3}{2} \right\}$ $= \frac{\text{N}}{10} \text{HI}$ obtained by decomposi- tion of a portion of nitrogen iodide into hydriodic acid and nitrogen.	Amount of nitrogen that should be obtained at 0° and 760 mm. calcu- lated from hydriodic acid in pre- vious column.	Amount of nitrogen actually measured at 0° and 760 mm.	Percentage of nitrogen iodide hy- drolyzed.	Percentage of nitrogen iodide de- composed by light.
2.96	1.48	43.16	41.68	31.12	30.8	3.42	96.58
2.24	1.12	48.72	47.60	35.54	35.26	2.29	97.71
4.08	2.04	62.63	60.59	45.24	44.61	2.45	97.55
4.08	2.04	55.65	54.11	40.39	39.73	2.76	97.24
7.76	3.88	75.28	71.40	53.31	53.01	3.82	96.18

The agreement is very close, but in every case the amount of nitrogen actually collected is slightly too small.

A loss must, however, necessarily occur because the solution of ammonia used in the reaction flask is saturated at the beginning of the experiment with air at the ordinary atmospheric pressure and consequently with nitrogen at four-fifths of an atmosphere. During the decomposition it becomes saturated with nitrogen at the atmospheric pressure.

*Experiment Demonstrating that Hydriodic Acid is Liberated during the Decomposition by Light.*

When nitrogen iodide decomposes under the influence of light all the iodine appears as hydriodic acid, which must neutralize an equivalent quantity of the ammonia in which it is suspended. In an experiment performed to demonstrate this conclusion, pure nitrogen iodide was allowed to decompose in light under a known excess of tenth-normal ammonia.

After the disappearance of the nitrogen iodide a known excess of tenth-normal sulphuric acid was added, and the free iodine representing the iodate estimated as usual by standard sulphite. The excess of sulphuric acid was now titrated by standard alkali and finally the total iodine in the nitrogen iodide used by tenth-normal silver nitrate.

$\frac{N}{10}$ $\text{NH}_3$ added. cc.	$\frac{N}{10} \frac{\text{H}_2\text{SO}_4}{2}$ required to neutralize $\text{NH}_3$ left free after the reaction.	$\frac{N}{10}$ $\text{NH}_3$ neutralized in the reaction = a.	$\frac{N}{10} \frac{\text{Na}_2\text{SO}_3}{2}$ required to react with $\text{HIO}_3$ produced in the hydrolysis.	$\frac{N}{10}$ $\text{HI}$ formed by action of sodium sulphite on the $\text{HIO}_3$ produced in the hydrolysis = $\frac{1}{6} \left\{ \frac{N}{10} \frac{\text{Na}_2\text{SO}_3}{2} \right\}$	$\frac{N}{10}$ $\text{NH}_3$ neutralized by nitrogen iodide hydrolyzed = b.	$\frac{N}{10} \text{AgNO}_3 = \frac{N}{10}$ $\text{I}$ in nitrogen iodide used.	$\frac{N}{10} \text{AgNO}_3 - \frac{1}{2} \left\{ \frac{N}{10} \frac{\text{Na}_2\text{SO}_3}{2} \right\} =$	$\frac{N}{10}$ $\text{HI}$ formed by decomposition of nitrogen iodide in $\text{N}$ and $\text{HI} = \frac{N}{10} \text{NH}_3$ that should be neutralized.	$(a-b) = \frac{N}{10}$ $\text{NH}_3$ actually neutralized by the $\text{HI}$ formed in the decomposition by light.
125.8	104.0	21.8	12.9	2.15	26.3	19.85	19.65		
188.7	156.0	32.7	20.3	3.38	39.6	29.45	29.32		

In column 7 is the amount of ammonia which should be neutralized in the decomposition. It is calculated from the hydriodic acid produced by the action of light. In column 8 is the ammonia actually neutralized. The agreement is sufficiently close. It is noteworthy that the percentages of nitrogen iodide hydrolyzed in these experiments are very high; viz., 24.5 and 25.6. The experiments were made in a warm room in December, and several days elapsed before the nitrogen iodide completely disappeared.

#### *Action of Light on Iodine Suspended in a Solution of Ammonia.*

In this experiment we were able to compare our results with the numbers given by Guyard. A weighed quantity of iodine was placed under 150 cc. of 3N-ammonia solution in the apparatus described above, and exposed to direct sunlight or to the light from a Welsbach incandescent burner when the former was not available. After the disappearance of all solid particles the evolved nitrogen was measured and the iodate and total iodine estimated, the latter by weighing as silver iodide.

Gram.	cc.	cc.	cc.	cc.	cc.	cc.	cc.
1.1486	= 90.8	45.4	7.6	3.8	41.6	31.05	30.45
$\begin{array}{l} \text{Weight of iodine used and num-} \\ \text{ber of cc. of a } \frac{N}{10} \text{ I solution cor-} \\ \text{responding to this.} \end{array}$							
$\begin{array}{l} \text{Half amount of iodine used =} \\ \text{amount converted into nitrogen} \\ \text{iodide and ammonium hypoiodite} \\ \text{as cubic centimeters of a } \frac{N}{10} \text{ I} \\ \text{solution.} \end{array}$							
$\frac{N}{10} \left( \frac{Na_2SO_3}{2} \right)$							
$\frac{1}{2} \left( \frac{N}{10} \frac{Na_2SO_3}{2} \right) = \frac{N}{10} \text{ I in nitro-}$							
$\text{gen iodide hydrolyzed and in am-}$							
$\text{monium hypoiodite.}$							
$\frac{1}{2} \left( \frac{N}{10} \text{ I used} \right) - \frac{1}{2} \left( \frac{N}{10} \frac{Na_2SO_3}{2} \right)$							
$= \frac{N}{10} \text{ I obtained by decomposition}$							
$\text{of a portion of the nitrogen iodide}$							
$\text{formed into hydriodic acid and}$							
$\text{nitrogen.}$							
$\begin{array}{l} \text{Amount of nitrogen that should} \\ \text{be obtained calculated from} \\ \text{amount of hydriodic acid pro-} \\ \text{duced as given in previous col-} \\ \text{umn at } 0^\circ \text{ and } 760 \text{ mm.} \end{array}$							
$\begin{array}{l} \text{Amount of nitrogen actually} \\ \text{measured at } 0^\circ \text{ and } 760 \text{ mm.} \end{array}$							

The agreement between the numbers in columns 6 and 7 is satisfactory and proves the correctness of the interpretation given above.

#### *Action of Light of Different Wave-lengths on Nitrogen Iodide.*

In these experiments solutions prepared according to Landolt's directions were used to obtain light belonging to given regions of the spectrum. Two Welsbach incandescent burners were employed as a source of light. The light from these was passed first through a condenser, then through the colored solution, and was finally reflected by a plane mirror on to the surface of crystalline nitrogen iodide mounted on a glass slide in 3N-ammonia. The slide itself was placed on a plane mirror. When light was allowed to fall on the nitrogen iodide decomposition began and, after the saturation of the liquid with nitrogen, bubbles of gas were seen to form on the crystals. It was possible to determine with great accuracy the instant at which these bubbles appeared. The time in seconds from the instant of exposure to light to the first appearance of bubbles was noted. This may be taken as inversely proportional to the intensity of the action of the light, assuming that the same amount of liquid surrounding the crystals is saturated in each case before the bubbles become visible.

When the slide was placed in a photographic dark room no bubbles of gas appeared in twenty minutes. In the diffused daylight which reached the slide in the apparatus, one hundred and eighty seconds elapsed before bubbles were seen.

The following table shows the time of exposure to different kinds of light, in seconds, before bubbles of gas appeared :

	First set of experiments.	Second set of experiments.
White light	14	14
Red "	48	49
Green "	90	92
Blue "	72	70
Indigo "	135	140

These results confirm Guyard's observation that the red end of the spectrum decomposes nitrogen iodide most readily, and that the action gradually becomes less as the wave-length of the light used diminishes. A secondary maximum, however, appears in the blue.

We have to thank Mr. F. F. Blackman, Fellow of St. John's College, Cambridge, for the use of his microscope and solutions, and for very kind assistance in these observations on the action of light.

CHEMICAL LABORATORY, ST. BARTHOLOMEW'S HOSPITAL AND COLLEGE, LONDON.

## FORMATION OF INDIGO FROM DIPHENYLDIKETOPIPERAZINE.

BY M. KUHARA AND M. CHIKASHIGE.

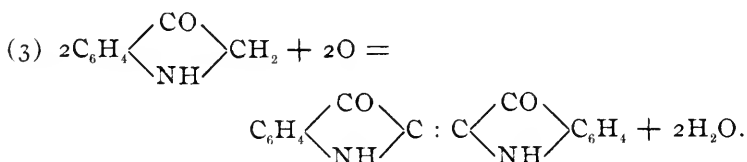
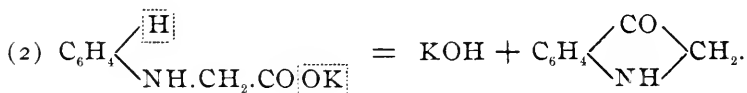
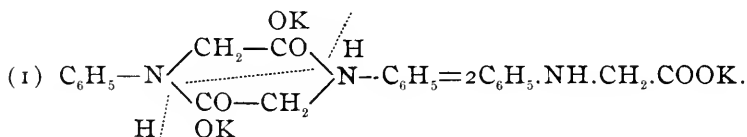
In the course of certain investigations on some complex compounds of the closed carbon-nitrogen nucleus, the authors saw an opportunity to try a new method for the formation of indigo. They believed that the compound diphenyldiketopiperazine,  $C_6H_5 \cdot N \begin{matrix} \diagup CO-CH_2 \\ \diagdown CH_2-CO \end{matrix} N \cdot C_6H_5$ , first prepared by

Abenius,<sup>1</sup> would split up on fusing with dry caustic potash into phenylglycocoll, which must instantly change by the further action of the alkali to pseudoindoxyl and finally the latter to indigo by oxygen, the last part of the reactions proceeding analogously to those of Heumann's synthesis.<sup>2</sup> The

<sup>1</sup> Ber. d. chem. Ges., **21**, 1665. The same compound was prepared by Hausdörfer by heating aniline, chloracetic acid, and sodium acetate, and called by him diphenyl- $\alpha$ - $\gamma$ -diacipiperazine.—Ber. d. chem. Ges., **22**, 1797.

<sup>2</sup> Ber. d. chem. Ges., **23**, 3043.

series of reactions which the authors supposed would take place, is represented by the following equations :



For the purpose of testing the authors' view, diphenyldiketopiperazine was prepared from monochloracetanilide,



according to Abenius' directions, and the compound thus obtained was fused with dry caustic potash, by which process indigo blue was found to be formed, so that we believe that our assumption has been realized.

### Experiments.

First a large quantity of monochloracetanilide was prepared according to the directions given by P. J. Meyer<sup>1</sup> from monochloracetyl chloride. As Abenius does not give the details of the process for preparing diphenyldiketopiperazine from monochloracetanilide, the authors proceeded in the following way: A molecular quantity of monochloracetanilide was boiled for about five minutes with a molecular quantity of caustic potash dissolved in absolute alcohol. Next, the potassium chloride precipitated was filtered and the alcohol removed from the filtrate by distillation. The residue, which consisted mainly of diphenyldiketopiperazine was washed with hydrochloric acid to remove the aniline formed, and finally dried with ether. The substance was then purified by re-

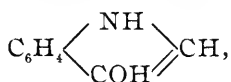
<sup>1</sup> Ber. d. chem. Ges., 8, 1152.



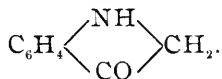
crystallization from alcohol, and the crystals thus obtained were found to melt at  $263^{\circ}$  as Abenius had observed.

On subjecting a mixture of a certain quantity of diphenyldiketopiperazine and a little more than an equal quantity of dry, powdered caustic potash in a glass vessel to fusion with sufficient care, the fused mass assumed finally a brownish-yellow color, while at the same time aniline and phenyl isocyanide were formed. The product, dissolved in water, instantly assumed a blue color, and in a short time a blue powder settled upon the bottom of the vessel. The blue coloring-matter, collected and dried, was tested for indigo. It was found to possess all the properties of indigo.

It will be remembered that some years ago Flimm<sup>1</sup> effected the synthesis of indigo by fusing monobromacetanilide,  $\text{CH}_2\text{Br}.\text{CONH}.\text{C}_6\text{H}_5$ , with dry caustic potash and subsequently oxidizing the aqueous solution of the product by air. The reactions in his process have, however, remained quite obscure hitherto, but have now, we believe, been made clear by the authors' synthesis. He states: "Indigo wird nicht direct gebildet, sondern als erstes Condensationsprodukt des Monobromacetanilids entsteht Indoxyl,



oder vielleicht ein Pseudoindoxyl der Formel

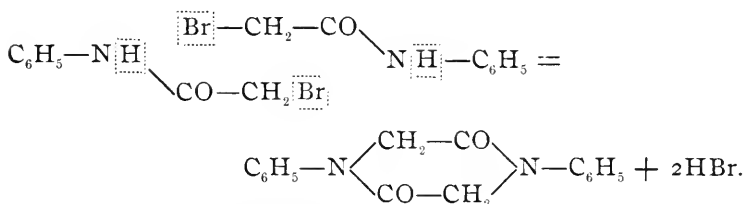


Dieses Zwischenglied geht durch Oxydation in Indigo über. Es ist mir nicht gelungen, dasselbe zu isoliren und rein darzustellen, da es äusserst unbeständig zu sein scheint. Besonders die Entstehung des Pseudoindoxyls hat die grösste Wahrscheinlichkeit für sich. Es tritt dann mit dem Brom ein Wasserstoffatom des Benzolkerns aus. Die Carbonylgruppe tritt an dessen Stelle, nämlich benachbart zum Stickstoff, und zwischen letzterem und der Methylengruppe findet einfache Bindung statt."

<sup>1</sup> Ber. d. chem. Ges. **23**, 57.

Heumann<sup>1</sup> also ventured to explain the nature of the reactions in Flimm's synthesis, and states: "Ehe aus jenem Körper (Monobromacetanilide) indess Pseudoindoxyl oder Indigo entstehen kann, musste zuerst eine Umlagerung zwischen den Gruppen CO und CH<sub>2</sub> erfolgen. Ob hierbei vielleicht als Zwischenprodukt das Bromid des Phenylglycocolls und, da Kali vorhanden ist, hieraus Phenylglycocoll resp. dessen Kaliumsalz entsteht, muss vorerst dahingestellt bleiben."

The explanations, both of Flimm and of Heumann, with regard to the nature of the molecular rearrangement, which consists apparently of the mutual exchange of the positions of the groups CO and CH<sub>2</sub>, are unsatisfactory. The authors have, however, found a more probable explanation in supposing that diphenyldiketopiperazine may possibly be formed from monobromacetanilide, as its first condensation-product, on fusing with dry caustic potash, the action of which is considered to be analogous to that of alcoholic potash, and that, as in the authors' synthesis, it may instantly split up into phenylglycocoll which is, in turn, transformed into pseudoindoxyl and this into indigo. The formation of diphenyldiketopiperazine from monobromacetanilide by the action of dry caustic potash is represented thus:



CHEM. LABORATORY, THE IMP. UNIVERSITY, KYOTO, JAPAN, March 24, 1900.

<sup>1</sup> Ber. d. chem. Ges., **23**, 3045.

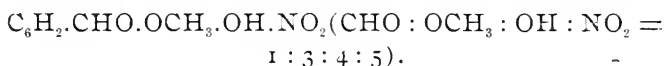
# THE ACTION OF NITRIC ACID ON VANILLIN.

BY WILLIAM B. BENTLEY.

## INTRODUCTION.

The investigation of this subject was undertaken in consequence of some unsuccessful attempts to oxidize the chlorvanillin prepared by A. E. Menke, to chlorvanillic acid. It was hoped that by regulating the action of dilute nitric acid it might be found possible to convert vanillin and its substitution-products into corresponding vanillic acids. The purpose of the experiment was entirely defeated by the unexpected action of dilute nitric acid. The reaction which apparently occurred first was an oxidation identical with that observed by Tiemann<sup>1</sup> when vanillin was boiled with a solution of ferric chloride, whereby a substance  $(C_6H_2CHO.OCH_3.OH)_2$ , by him called dehydrodivanillin, was produced. Concurrently with this reaction, but proceeding more slowly, was a substitution of a nitro group in the ring. This action was rather surprising, as the nitration took place even when the strength of the nitric acid did not exceed 5 per cent. In addition to these two compounds, perhaps by subsequent action of the nitric acid on nitrovanillin, dinitroguaiacol was formed and in minute quantity another compound, the identity of which it was impossible to determine.

Nitrovanillin was converted into dinitroguaiacol by further action of nitric acid and its constitution thus shown to be



The position of the hydrogen in the vanillin molecule which is most easily substituted is therefore in the meta relation to the aldehyde and oxymethyl groups, and ortho to the hydroxyl group. Nitrovanillin was also oxidized to nitrovanillic acid, a compound previously described by Weselsky and Benedikt.<sup>2</sup> Attempts were made to obtain amidovanillin but, although the compound was obtained as a flocculent white precipitate, it blackened immediately, and all efforts to obtain

<sup>1</sup> Ber. d. chem. Ges., 18, 3493.

<sup>2</sup> Monatsh. Chem., 3, 392.

it in pure condition failed. Various experiments were made with a view to carrying the nitrovanillin by reduction and subsequent treatment by the Sandmeyer reaction to chlorvanillin, but they were unsuccessful. The organic compound seemed to be entirely lost in the process.

#### EXPERIMENTAL PART.

##### *Nitrovanillin.*

Vanillin in lots of about 2 grams each was dissolved in water by warming 1 part of vanillin with 80 of water. To this solution was added 8 parts by volume of common strong nitric acid, sp. gr. 1.38. The mixture was digested at 50°, which caused a strong yellow color to be developed in the solution, accompanied presently by the separation of a dirty white precipitate, the color of which became rapidly darker. In one experiment the precipitate was filtered out as soon as any considerable quantity had accumulated. After further digestion another precipitate appeared, and this was separated by filtration, after which the digestion was continued until precipitation was at an end. The entire period was about two hours. The first portion was found to consist of about 80 per cent dehydrodivanillin, while the second was 30 per cent, and the last portion, which was about two-thirds of the whole precipitate, contained but 10 per cent dehydrodivanillin. The results show that, although the formation of nitrovanillin begins immediately, the greater part of this compound appeared only after some time while dehydrodivanillin was formed almost entirely at the very outset. The yield of nitrovanillin in this reaction was about 50 per cent of the weight of vanillin taken, while that of dehydrodivanillin was about 20 per cent. The precipitate was washed once or twice with water, but this treatment should not be carried too far as nitrovanillin is somewhat soluble in water. The residue is next extracted with boiling alcohol until the extract is no longer yellow. This extraction can be made much quicker by substituting boiling glacial acetic acid for alcohol, as the compound is freely soluble in hot acetic acid but only fairly soluble in alcohol. The nitrovanillin was recrystallized from alcohol or

acetic acid until it showed the constant melting-point,  $176^{\circ}$ .

The introduction of a nitro group by nitric acid of so great dilution seemed so unusual that the compound was prepared by a more general method. Vanillin was dissolved in glacial acetic acid and an acetic acid solution of the calculated quantity of fuming nitric acid was added. The mixture became very red and almost immediately precipitated nitrovanillin in amount only slightly less than theory demands. This compound was essentially pure, as it was shown that by recrystallization its melting-point was very little changed. The substance so obtained is identical in every respect with that prepared with dilute acid, as before described.

In the analysis of this compound the ordinary combustion methods did not succeed, although repeated trials were made and all possible precautions were observed. The identity of the compound was so unmistakably indicated by the methods of preparation that this evidence, together with some determinations of nitrogen by the Kjeldahl method and analytical results with the potassium salt as described below, were taken as sufficient proof of its composition.

I. 0.9961 gram of the substance dissolved in sulphuric acid, reduced with sodium thiosulphate, and treated according to the method of Kjeldahl, yielded ammonia sufficient to neutralize 47.31 cc. decinormal acid.

II. 1.0197 grams of substance treated as above yielded ammonia sufficient to neutralize 47.78 cc. decinormal acid.

III. 1.1146 grams of substance yielded ammonia sufficient to neutralize 53.66 cc. decinormal acid.

	Calculated for $C_6H_2CHO.OCH_3.OH.NO_2$ .	I.	Found. II.	III.
N	7.11	6.65	6.56	6.74

As results obtained by this method are usually low when nitrogen is present in the oxidized condition these results seem admissible.

Nitrovanillin, in the pure state, melts at  $176^{\circ}$  and crystallizes best from glacial acetic acid in which it dissolves freely when hot and but slightly when cold. It is less soluble in hot alcohol, from which it separates, on cooling, in crystals similar to those from acetic acid, only smaller and more poorly

defined. The crystals are pale yellow plates, apparently of the hexagonal system. The solution gives a yellow stain somewhat similar to that of picric acid. In methyl alcohol it is somewhat more soluble than in ethyl. It is soluble in chloroform and carbonic disulphide. It dissolves but little in acetone, is practically insoluble in ether. It dissolves to a limited extent in water and in hydrochloric and sulphuric acids. With nitric acid it gives dinitroguaiacol as described below. Nitrovanillin probably forms salts with all the basic elements. It is sufficiently acid to dissolve calcium carbonate, forming the yellow calcium salt. Solutions of salts of the basic elements were tested with a cold saturated solution of the potassium salt. In most cases a yellow precipitate was produced, which precipitate dissolved if the solution was heated. In the following cases no precipitate was produced, owing, probably, to the solubility of the salts which would have been formed: The salts of the alkalis, magnesium, manganese, cobalt, nickel, mercury. Chromium formed a light-green precipitate, copper a greenish-yellow, and lead a voluminous yellow precipitate which seemed only slightly soluble in hot water. The substance is not liberated from its alkaline salts by carbon dioxide nor by sulphuretted hydrogen but is precipitated by acetic acid.

*Potassium Salt of Nitrovanillin.*—To establish further the identity of the nitrovanillin the potassium salt was prepared by dissolving nitrovanillin in dilute potassium hydrate by the aid of heat. As the salt dissolves easily in hot water and but little in cold, the compound was easily purified. It was dried at  $100^{\circ}$  and analyzed by dissolving in water, precipitating the organic matter with sulphuric acid, and evaporating the solution of potassium sulphate which had been filtered from nitrovanillin.

I. 0.2465 gram of the salt gave, when treated as above, 0.0907 gram of potassium sulphate.

II. 0.4090 gram of the salt gave 0.1516 gram potassium sulphate.

	Calculated for	Found.	
	$C_6H_2CHO.OCH_3.OK.NO_2$	I.	II.
K	16.63	16.52	16.64

It was observed that in drying the crystals they underwent considerable change in appearance, which seemed to indicate that they originally contained water of crystallization. To determine the amount of this water a freshly crystallized specimen was dried with filter-paper and then exposed in air for two hours. The crystal water was driven off in the steam oven. Although satisfactory results could not be secured because water was slowly lost at ordinary temperature, and on account of the nature of the crystal mass, perfect removal of adhering water did not seem to be effected by pressing with filter-paper. The following results leave but little doubt, however, that there was a single molecule of crystal water.

I. 1.0788 grams of the crystals, dried at the temperature of the steam oven, lost 0.0721 gram.

II. 1.3178 grams of crystals lost 0.0878 gram.

	Calculated for (C <sub>6</sub> H <sub>2</sub> CHO.OCH <sub>3</sub> .OK.NO <sub>2</sub> )H <sub>2</sub> O.	I.	Found. II.
H <sub>2</sub> O	7.11	6.68	6.66

The potassium salt of nitrovanillin separates from its hot aqueous solution in a compact mass of long fibrous crystals. These are of an extremely bright orange-red color when hydrous, but on losing water they become a darker red. The salt dissolves freely in hot water and much less in cold, and its solubility is much decreased by the presence of potassic hydrate. It dissolves quite readily in hot ethyl alcohol and only slightly in cold. In methyl alcohol it is more soluble than in ethyl when cold, and is not separated from this solvent when the hot solution is cooled. It is slightly soluble in acetone, very slightly in ether, and insoluble in benzol and chloroform.

#### *Dehydrodivanillin.*

The writer is unable to present analytical proof that the insoluble compound obtained, as above described, is dehydrodivanillin, because no means of obtaining satisfactory results were found, although much time was spent in the effort. As the compound is insoluble in all common organic solvents the attempt was made to purify it by dissolving in potassic hydrate and precipitating with carbon dioxide. This process

was repeated many times, but as it melts above  $300^{\circ}$  there was no proof of the purity of the samples analyzed and the results seem to show that this method was not sufficient. That the compound was really dehydrodivanillin it seems there is little doubt. In the first place, the method of preparation was similar to that of Tiemann,<sup>1</sup> the very dilute nitric acid replacing aqueous ferric chloride as an oxidizing agent. In the second place, the compound melts above  $390^{\circ}$ , and has in every other respect the somewhat unusual properties of dehydrodivanillin. It was compared with the compound made by action of aqueous ferric chloride and no difference between the two samples was observed. Some efforts were made to prepare and analyze the sodium salt. The compound was boiled with an insufficient quantity of an alcoholic solution of sodic ethylate, and the unaltered compound filtered out. The solution of the sodium salt was then evaporated, and the salt separated either by crystallization or by complete evaporation. In one determination of sodium the percentage found was in close agreement with that calculated for the disodium salt of dehydrodivanillin, but this result had to be rejected as untrustworthy because subsequent determinations gave too low results, indicating that the disodium salt contained also some of the monosodium salt. As there seemed to be no way of obtaining the disodium salt in a condition of purity the subject was abandoned.

*The Action of Nitric Acid on Nitrovanillin.*

The dilute nitric acid mother-liquor from which the nitrovanillin was filtered, as described above, had a strong yellow color showing that some compound soluble in water was also formed. The isolation of this compound proved rather troublesome. When the large volume of water in which it was dissolved was evaporated by heat, the nitric acid remaining, oxidized the organic matter to oxalic acid. An ineffectual attempt was made to prevent this by reducing the nitric acid with alcohol. A more satisfactory result was secured by neutralizing the liquid with potassic hydrate and evaporating the neutral solution to dryness. The separation of the potassium

<sup>1</sup> Ber. d. chem. Ges., 18, 3493.



nitrate from the potassium salt of the organic compound was, however, a matter of no little difficulty as the two salts crystallized together, being apparently isomorphous. It was indeed found impossible in this way to obtain any considerable quantity of the compound, though a small amount was obtained by the following method: The dry residue was repeatedly extracted with strong alcohol, which dissolved most of the organic salt and considerable quantities of the nitrate. The alcoholic solution was then freed from potassium by precipitation with dilute sulphuric acid. In this way enough of the compound was secured to show that it melted at  $123^{\circ}$ , and was probably the dinitroguaiacol prepared by Hertzog.<sup>1</sup> Fortunately, it was found that if the action of nitric acid on vanillin was managed in a manner differing somewhat from the one described above, the compound could be obtained without much trouble. The vanillin was dissolved in water as before, but the volume of water was doubled so that the solution could be cooled without the separation of vanillin. After cooling, the nitric acid was added and the mixture was digested in the cold for several days. The products were the same as before, except that the dinitroguaiacol was found in greater quantity, probably on account of the conversion of nitrovanillin to dinitroguaiacol by more prolonged action of nitric acid. The dehydrodivanillin was in this process precipitated in a slimy condition, which rendered the extraction of the nitrovanillin difficult. After separating the precipitated matter, the acid liquid was allowed to evaporate spontaneously, when the dinitroguaiacol separated out in some quantity. It was recrystallized from dilute alcohol until it showed the constant melting-point  $123^{\circ}$ . To be sure of its identity it was analyzed with the following result:

0.1783 gram of the substance gave, on combustion, 20.9 cc. nitrogen measured at  $20^{\circ}$  and 727 mm. pressure.

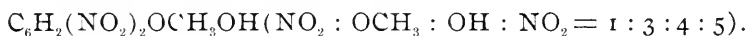
	Calculated for $C_6H_2(NO_2)_2OCH_2OH$ .	Found.
N	13.08	12.81

It was also shown that dinitroguaiacol can be made from nitrovanillin by the action of nitric acid, and there seems no

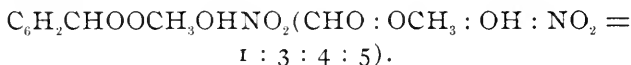
<sup>1</sup> Monatsh. Chem., 3, 825.

reason to think that the dinitroguaiacol obtained by the action of nitric acid on vanillin was not the product of a second reaction between the nitric acid and the nitrovanillin first formed. Nitrovanillin was warmed with water containing a little acetic acid to promote solubility and 2 or 3 molecules of nitric acid were added for each molecule of nitrovanillin present. On cooling, dinitroguaiacol separated out and was recognized by its melting-point and other properties. The quantity obtained in this process was about one-half the nitrovanillin used.

The conversion of nitrovanillin into dinitroguaiacol determines the structure of nitrovanillin for Hertzigs,<sup>1</sup> reasoning by analogy between the behavior of triamidophenol and that of diamidoguaiacol (obtained by reduction of dinitroguaiacol), concludes that dinitroguaiacol has the structure.



This makes it evident that the  $\text{NO}_2$  group standing at 5 was the one in nitrovanillin, while the other had displaced the  $\text{CHO}$  group of nitrovanillin when this latter compound was acted upon by nitric acid. The constitution of nitrovanillin is therefore



In neutralizing the nitric acid for the purpose of obtaining the dinitroguaiacol by the method mentioned above, it was observed that a slight excess of alkali caused the liquid to become a deep blood-red. Attempts were made to isolate the substance which gave this reaction by precipitating with acetate of lead. By this process a rather voluminous brown precipitate was produced and the blood-red color entirely disappeared, leaving the solution orange-red, the color of the potassium salt of dinitroguaiacol. Although this precipitate was repeatedly collected and treated with sulphuretted hydrogen no organic product was ever obtained.

#### *Oxidation of Nitrovanillin.*

In the earlier attempts to oxidize nitrovanillin, very unsat-

<sup>1</sup> Monatsh. Chem., 3, 825.

isfactory results were obtained, because an excess of the oxidizing agent, alkaline permanganate, effected the complete destruction of the molecule. No means was found of judging from the color of the solution when the oxidation had proceeded far enough. The desired amount of oxidation was finally obtained by using a measured volume of roughly standardized permanganate solution. The oxidizing power of the permanganate was determined by titrating against an acid solution of ammonio-ferrous sulphate and allowing that the oxidizing power in alkaline solution was three-fifths that in acid solution. By this means it was estimated that 1 gram of nitrovanillin required  $33\frac{1}{3}$  cc. of permanganate solution saturated at ordinary temperature. The process was conducted as follows: 2 grams of nitrovanillin were dissolved in a slight excess of potassic hydrate. To this solution were added 80 cc. of the permanganate solution, and the mixture was digested at ordinary temperature. The red color of the nitrovanillin salt was obscured by the purple of the permanganate which presently became green and finally yellow. The mixture was then heated to prevent any of the potassium salt of nitrovanillic acid from remaining enclosed in the precipitate of oxides of manganese, and the latter substance was filtered out. The yellow solution thus obtained was acidified with sulphuric acid which precipitated a portion of the organic matter, and the remainder was extracted with ether. It was found impossible to obtain anything by evaporation, as the nitrovanillic acid was either volatilized with steam or more likely decomposed by the hot acid. The product obtained, in spite of the excess of permanganate used, contained a considerable quantity of unaltered nitrovanillin, from which it was found difficult to separate it by crystallization. Fortunately, nitrovanillic acid is very readily soluble in ether, while nitrovanillin is almost insoluble in this solvent. The crude product which melted at about  $190^{\circ}$  was therefore treated with ether, and the soluble part further purified by recrystallization, while the soluble portion was again oxidized. As a crystallizing medium, dilute alcohol, which was first used, proved unsatisfactory, as the compound separated in very poor crystals and their appearance was no criterion of their purity.

The compound crystallized well from glacial acetic acid, and the compound was readily purified by use of this solvent. The pure compound melted at  $216^{\circ}$ – $216^{\circ}.5$ . Its identity was confirmed by the following analyses :

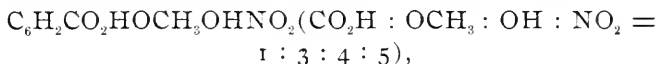
I. 0.1833 gram of the substance gave, on combustion, 0.0653 gram  $H_2O$ , and 0.3012 gram  $CO_2$ .

II. 0.1359 gram of the substance gave, on combustion, 0.0518 gram  $H_2O$ , and 0.2242 gram  $CO_2$ .

III. 0.1826 gram of the substance gave, on combustion, 11.73 cc of N at  $20^{\circ}.5$  and 730.85 mm. pressure.

	Calculated for $C_6H_2CO_2HOCH_2OHNO_2$ .	I.	Found. II.	III.
C	45.07	44.81	44.99	....
H	3.29	3.96	4.23	....
N	6.57	....	....	7.04

This compound, which must have the constitution



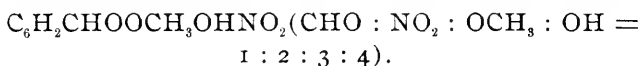
seems to differ in its properties from the nitrovanillic acid described by Weselsky and Benedikt<sup>1</sup> only in its melting-point, their compound melting at  $202^{\circ}$  instead of  $216^{\circ}$ .

The difficulties encountered in the preparation of pure nitrovanillic acid suggest a possible explanation of the low melting-point obtained by Weselsky and Benedikt. As their compound was made by oxidation of nitro Eugenol with permanganate, nitrovanillin was in all probability an intermediate product. The experiments made by the writer show in the first place that it is improbable that the oxidation was carried to such a point that all the nitrovanillin was converted to the acid. In the second place, it is difficult, if not impossible, to separate nitrovanillic acid from nitrovanillin by crystallization. The probability seems to be that their compound contained a trace of nitrovanillin. By nitration of acetylvanillic acid and subsequent saponification Tiemann and Matsmoto<sup>2</sup> obtained a nitrovanillin in which the nitro group occupied the ortho position with reference to the carboxyl instead of the meta position as it does here. It is perhaps in-

<sup>1</sup> Monatsh. Chem., 3, 392.

<sup>2</sup> Ber. d. chem. Ges., 9, 944.

teresting to note that the nitro group enters vanillin and eugenol at a point different from that which it enters in acetylvanillic acid. That this difference is due to the influence of the acetyl group is proved by the fact that Pschorr and Sumuhann,<sup>1</sup> by action of nitric acid on acetylvanillin, got a nitro derivative which yields nitrovanillin of the constitution

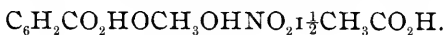


For the sake of possible comparison the writer adds the properties of the compound as he observed them. Nitrovanillic acid crystallizes from dilute alcohol in small, yellow needles, from acetic acid in well developed plates belonging apparently to the monoclinic system. It is quite soluble in cold ethyl or methyl alcohol; also in acetone or ether; soluble in hot glacial acetic acid; very sparingly in cold; it dissolves slightly in water or chloroform, very slightly in carbon disulphide; it dissolves in sulphuric or nitric acid and is decomposed by the latter. Hydrochloric acid has apparently no action on it. The crystals from acetic acid are light-yellow and transparent, and contain acetic acid. The acetic acid is readily lost and the crystals fall to a powder, which is much darker than the crystals. An effort was made to determine the acetic acid in these crystals. As acetic acid is lost at ordinary temperature, the results were not wholly satisfactory. The substance was crystallized, dried between filter-papers, and the acetic acid determined by heating in the steam oven. The results were as follows:

I. 0.9618 gram of the crystals lost 0.2794 gram, or 29.05 per cent.

II. 0.5506 gram of the crystals lost 0.1610 gram, or 29.23 per cent.

One molecule of acetic acid would require 21.98 per cent, while 1.5 molecules require 29.70 per cent. The results seem to indicate fairly well that the crystals obtained from an acetic acid solution of nitrovanillic acid have the composition




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<sup>1</sup> Ber. d. chem. Ges., 32, 3405.

# ON THE EFFECT OF OXIDIZING AGENTS ON THE REDUCTION OF MERCURIC CHLORIDE BY OXALIC ACID.

BY J. H. KASTLE AND W. A. BEATTY.

It has been shown by Amato<sup>1</sup> and also in this laboratory<sup>2</sup> that the chemical effect of light is exerted only above certain temperatures, or better, perhaps, between certain rather narrow limits of temperature. In seeking for another reaction on which to test this point, it occurred to one of us (Kastle) that perhaps Eder's chemical photometer, which depends on the reduction of mercuric chloride by ammonium oxalate in the sunlight, and which is influenced to a considerable extent by temperature, might furnish a chemical reaction well suited for our purpose.<sup>3</sup>

In attempting to follow the progress of this reaction by determining by means of potassium permanganate the quantity of oxalate remaining unaltered, it was observed that a very rapid reduction of the mercuric chloride occurred on adding even a few drops of the solution of permanganate. In fact, it soon became apparent that it would be impossible to measure the rate of change in this way. The accelerating effect of the permanganate on the progress of the reaction proved to be so remarkable and interesting that the problem of measuring the effect of light on the reaction at different temperatures was temporarily abandoned in order that the acceleration produced by the permanganate and other oxidizing agents might be more thoroughly studied. In what follows, unless expressly stated to the contrary, solutions of ammonium oxalate and mercuric chloride of the following concentrations were employed: 40 grams of ammonium oxalate per liter, and 50 grams of mercuric chloride per liter.

In our experiments these solutions were mixed immediately before using in the proportion of two volumes of the oxalate solution to one volume of the chloride. Unless stated to the contrary, 10 cc. of the oxalate with 5 cc. of the chloride solu-

<sup>1</sup> Gazz. chim. Ital., **14**, 57.

<sup>2</sup> This JOURNAL, **20**, 159-163; J. Am. Chem. Soc., **21**, 268-272.

<sup>3</sup> Ber. d. chem. Ges. **13**, 166.

tion were employed in each experiment. The experiments were conducted in thin-wall color-tubes, similar in shape to nesslerizing cylinders. In order to determine something as to the extent of the acceleration produced by potassium permanganate on the reaction, the following experiment was tried :

Two tubes were prepared : each of these containing 10 cc. of ammonium oxalate, together with 5 cc. of mercuric chloride. To one of them 1 drop of a N/100 solution of potassium permanganate was added. The two tubes were then placed side by side in the direct sunlight and allowed to remain thus exposed for ten minutes. At the end of this time they were removed from the direct sunlight and quickly filtered. The precipitates of mercurous chloride thus obtained were heated with 10 cc. of caustic potash solution and 0.5 gram of zinc dust. The two solutions were then filtered through asbestos and the filtrates titrated with N/10 silver nitrate. In this way the amount of mercurous chloride precipitated in each of the two tubes was determined. In the tube to which 1 drop of N/100 permanganate had been added, 28.2 per cent of the mercuric chloride had been reduced ; whereas, in the tube to which no permanganate had been added, only 3.48 per cent of mercuric chloride had been reduced. Thus, it was shown that about 0.016 mgm. of potassium permanganate in 15 cc. of solution was sufficient to produce a reduction of mercuric chloride by ammonium oxalate eight times faster than when the oxalate and mercuric chloride were allowed to react alone. In order to make sure that only mercuric chloride was precipitated in the presence of the permanganate, some of the precipitate thus obtained was dried and the chlorine in it determined with the following result :

	Calculated for HgCl.	Found.
Cl	15.04	15.16

The attempt was then made to determine the smallest quantity of potassium permanganate capable of producing an acceleration of the reaction. This was accomplished in the following manner :

A number of tubes were prepared containing 10 cc. of am-

monium oxalate together with 5 cc. of mercuric chloride. Two of these tubes were then placed in the direct sunlight, and to one of them 1 drop of a solution of potassium permanganate of known strength was added. The time required for the formation of the precipitate of mercurous chloride, together with the quantity of the precipitate produced in each tube in a given time, afforded a rapid, though rough, method of measuring the acceleration produced. The following is a summary of the results obtained :

1 drop of N/100  $\text{KMnO}_4$ <sup>1</sup> = 0.00001578 gram  $\text{KMnO}_4$ , greatly accelerated the reduction.

1 drop of N/2500  $\text{KMnO}_4$  = 0.00000063 gram  $\text{KMnO}_4$ , greatly accelerated the reduction.

1 drop of N/20000  $\text{KMnO}_4$  = 0.000000078 gram  $\text{KMnO}_4$ , considerably accelerated the reduction.

1 drop of N/40000  $\text{KMnO}_4$  = 0.000000039 gram  $\text{KMnO}_4$ , very perceptibly accelerated the reduction.

1 drop of N/80000  $\text{KMnO}_4$  = 0.0000000195 gram  $\text{KMnO}_4$ , slight but perfectly perceptible acceleration.

1 drop of N/160000  $\text{KMnO}_4$  = 0.00000000975 gram  $\text{KMnO}_4$ , very slight acceleration.

It will be seen, therefore, that about 0.00000000975 gram of  $\text{KMnO}_4$ , in 15 cc. of solution, is about the smallest quantity of this substance capable of accelerating the reduction of mercuric chloride by ammonium oxalate under the most favorable conditions.

The acceleration by permanganate was found to be greatest in direct sunlight. In diffused light and in gaslight, however, it was still very marked, but in the dark the accelerating effect of the permanganate was observed to be very much impaired. Results similar to the above were obtained with a mixture of potassium permanganate and sulphuric acid. In this case, however, the acceleration was not quite so pronounced in certain of the experiments, indicating that the free sulphuric acid exerted a retarding action on the reduction. Other acids, such as hydrochloric and nitric, were also found to retard the reduction to a noticeable extent.

<sup>1</sup> The concentration of the solution of permanganate is based upon that of a decinormal solution of this salt, containing 3.156 grams per liter.



Ferric chloride was also found to accelerate the reduction in direct sunlight, as may be seen from the following :

1 drop of N/100  $\text{FeCl}_3$  = 0.00008125 gram  $\text{FeCl}_3$  in 15 cc. solution, caused great acceleration.

1 drop of N/2000  $\text{FeCl}_3$  = 0.00004062 gram  $\text{FeCl}_3$  in 15 cc. solution, produced great acceleration.

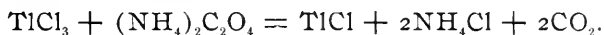
1 drop of N/4000  $\text{FeCl}_3$  = 0.00002031 gram  $\text{FeCl}_3$  in 15 cc. solution, acceleration plainly perceptible.

1 drop of N/8000  $\text{FeCl}_3$  = 0.00001016 gram  $\text{FeCl}_3$  in 15 cc. of solution, very slight acceleration.

About 0.001 mgm. of ferric chloride in 15 cc. solution is therefore believed to be the smallest quantity of this substance that can cause acceleration under the most favorable conditions. Still other oxidizing agents were found to greatly accelerate the reduction of mercuric chloride by ammonium oxalate in the sunlight. Among them may be mentioned the following : Iron alum, auric chloride, platinic chloride, thallic chloride, chrome alum, uranium nitrate, iodic acid, potassium bromate, ammonium persulphate, chlorine water, etc. On the other hand, a few of them such as chromic acid, potassium chromate, and dichromate, were found to retard the change.

*Reduction of Thallic Chloride by Ammonium Oxalate in the Sunlight.*

Thallic chloride is rapidly reduced by ammonium oxalate in the sunlight with the formation of thalrous chloride, ammonium chloride, and carbon dioxide :



This reaction is altogether analogous to the reduction of mercuric chloride by ammonium oxalate, and like the latter it has been found to be greatly accelerated by other oxidizing agents. A solution of thallic chloride was prepared containing 87.2 grams  $\text{TlCl}_3$  per liter. Several tubes were then prepared containing 10 cc. of the solution of ammonium oxalate (40 grams of ammonium oxalate per liter) and 5 cc. of the thallic chloride solution. One of these tubes was placed in diffused light and a second one in the direct sunlight. The reduction

in both cases was considerable. In the tube exposed to direct sunlight, however, it was greatly in excess of that in the diffused light. Two tubes containing a mixture of thallic chloride and ammonium oxalate were placed in the direct sunlight and a drop of N/20 ferric chloride added to one of them. The most remarkable acceleration in the reduction of the thallic chloride was thus brought about. In the same way, 1 drop of N/100 potassium permanganate was observed greatly to accelerate the reduction.

While certainly very remarkable, these are by no means the only instances in which oxidation or reduction is greatly accelerated by the presence of other substances, usually oxidizing agents, and not immediately concerned in the change. According to Harcourt<sup>1</sup> chromic acid only oxidizes oxalic acid in the cold in the presence of manganous sulphate. Lothar Meyer<sup>2</sup> and others have found that the oxidation of solutions of sulphur dioxide in water by the oxygen of the air is greatly accelerated by certain metallic salts, such as the sulphates of manganese, copper, iron, and cobalt. Jorissen<sup>3</sup> has shown that boric and sulphuric acids increase the velocity of oxidation of oxalic acid in the light. He made the further interesting observation in this connection that while manganese sulphate promotes the oxidation of oxalic acid in the dark, it actually acts as a preservative of it in the light. Quite recently, Jorissen and Reicher<sup>4</sup> have shown that in diffused light the oxidation of oxalic acid is accelerated by the sulphates of iron, chromium, cerium, thorium, and erbium; also by sodium fluoride, and by manganese sulphate, acetate, butyrate, benzoate, and oxalate.

On the other hand, potassium, magnesium, and yttrium sulphates exert no accelerating influence on the oxidation. In sunlight manganese oxalate, sulphate, acetate, butyrate, and benzoate increased the rate of oxidation. According to these observers, the acceleration depends on the nature of the catalytic agent, and increases with its concentration. Further, the acceleration produced by manganese salts cannot be ac-

<sup>1</sup> British Association, 34th Meeting, 1864.

<sup>2</sup> Ber. d. chem. Ges., 20, 3058.

<sup>3</sup> Ztschr. angew. Chem. (1899), 521-525.

<sup>4</sup> Ztschr. phys. Chem. (1899), 31, 142-163.

counted for by the formation of manganese oxalate, for the reason that this substance is more slowly oxidized than oxalic acid itself. Richardson<sup>1</sup> has made the interesting observation that in the sunlight and in the presence of an excess of oxygen, hydrogen peroxide is produced in the oxidation of oxalic acid.<sup>2</sup> He also found that hydrogen peroxide accelerates the oxidation of oxalic acid by oxygen gas in the light. In view of the great diversity of these phenomena, it is not an easy matter to frame an hypothesis as to the cause of the acceleration of such oxidations which would be applicable to all cases. Perhaps the best explanation that can be given of such processes at present is that advanced by Lothar Meyer<sup>3</sup> to account for the accelerating influence of such salts as manganoous sulphate on the oxidation of sulphurous acid by gaseous oxygen. According to him, the salt causing the acceleration simply acts as a carrier of oxygen, and the part played by such salts is quite analogous to that taken by such substances as ferric chloride and other chlorine carriers in processes of substitution. In the same way, the part played by other oxidizing agents, such as potassium permanganate, ferric chloride, and thallic chloride in accelerating the oxidation of ammonium oxalate by mercuric chloride in the sunlight might also be explained. When ferric chloride, for example, is added to a solution of ammonium oxalate and mercuric chloride, it seems probable, at least, that the following changes would occur :

1. Reduction of ferric chloride to ferrous chloride by the ammonium oxalate.
2. Oxidation of the ferrous chloride to ferric chloride by the mercuric chloride.
3. Oxidation of the ammonium oxalate by the mercuric chloride.

It has been shown in most cases, at least, that the substances causing the acceleration of the change under discus-

<sup>1</sup> J. Chem. Soc. (London), 65, 467 (1894).

<sup>2</sup> Manchot has recently observed the formation of hydrogen peroxide in the oxidation of such substances as oxanthrol in alkaline solutions by atmospheric oxygen. —J. Chem. Soc. (London), May (1900), 300. And still more recently Engler has proved the formation of hydrogen peroxide in a large number of oxidations. —Ber. d. chem. Ges., 33, 1090.

<sup>3</sup> Ber. d. chem. Ges., 20, 3058.

sion are themselves capable of being reduced by the ammonium oxalate. It should be noticed in this connection, however, that at certain concentrations ferrous chloride is not oxidized by mercuric chloride, even in the sunlight. The impossibility of such a reaction, however, does not necessarily preclude the idea that this substance may act as a carrier of oxygen in the reduction of mercuric chloride by ammonium oxalate. In solution with ammonium oxalate, mercuric chloride must be in an extremely unstable state. It is therefore conceivable that in this condition it might be easily reduced by a substance altogether incapable of reducing it in its pure aqueous solutions. Or, looked at from a slightly different standpoint, the reducing agents produced in the reaction, such as ferrous chloride, etc., although incapable of reducing mercuric chloride directly themselves, might render it more unstable by their presence, and hence more readily reducible by the ammonium oxalate.

Quite recently, in fact since the above was written, one of us (Kastle) has succeeded in showing by means of the titanous acid reaction, that hydrogen peroxide is produced in small quantities, at least, in the oxidation of oxalic acid by potassium permanganate in the sunlight. As to just what bearing, if any, this observation may have on this problem here under discussion remains to be seen.

STATE COLLEGE OF KENTUCKY,  
LEXINGTON, May, 1900.

# AMERICAN CHEMICAL JOURNAL

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Contributions from the Sheffield Laboratory of Yale University.

## LXXVI.—ON THE BEHAVIOR OF ACYLTHIONCAR- BAMIC ESTERS WITH ALKYL IODIDES AND AMINES: BENZOYLIMIDOTHIOCAR- BONIC ESTERS, ACYCLIC BEN- ZOYLPSEUDOUREAS AND BENZOYL- UREAS.

BY HENRY L. WHEELER AND TREAT B. JOHNSON.

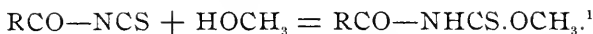
In this paper we describe the results of an examination of some acetyl and benzoyl thioncarbamic esters as regards their behavior with alkyl iodides and with organic bases. This examination led us to the investigation of a series of benzoyl-

imidothiocarbamic esters,  $C_6H_5CO-N=C \begin{matrix} \swarrow SR \\ \searrow OR \end{matrix}$ , acylpseudo-

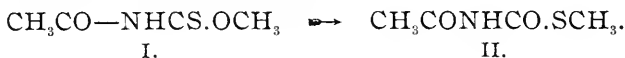
urea ethers,  $C_6H_5CO-N=C \begin{matrix} \swarrow NRR' \\ \searrow OR \end{matrix}$ , and benzoylureas,

$C_6H_5CONHCONRR'$ , a preliminary account of which is also given.

The acylthioncarbamic esters are prepared by the union of acyl rhodanides with alcohols:



We find that these compounds have little tendency to undergo molecular rearrangement with alkyl iodides, a fact which is probably due to the negative character of the molecules. We observed that a rearrangement took place only in the case of the acetyl and benzoyl methyl esters when warmed, within narrow limits, with methyl iodide:



The same thiol compound (II) was obtained by warming methyl thiolcarbamate,  $\text{H}_2\text{NCO.SCH}_3$ , with acetic anhydride on the water-bath, in the same way that Andreocci<sup>2</sup> found that xanthogenamide may be acetylated, this being the best method for the preparation of the acetylthioncarbamic esters.

These results show that the compounds formed by the union of acyl rhodanides with alcohols have the thion structure, I, which was assigned to them by Miquel<sup>3</sup> and Dixon,<sup>4</sup> and not the thiol structure as represented, subject to interrogation, in Beilstein's "Handbuch."<sup>5</sup>

We find that methyl benzoylthioncarbamate reacts more readily with chloracetic acid than with alkyl iodides, giving benzoylcarbaminthioglycollic acid:



In previous papers it has been shown that such thioncarbamic esters as have a more or less positive nature,<sup>6</sup> especially the phenylthioncarbazine esters,



readily react with alkyl halides and with compounds of a negative character; while, on the other hand, with organic bases they proved to be quite inert.

We now find in the case of the negative benzoylthioncarbamic esters,  $\text{C}_6\text{H}_5\text{CO.NHCS.OR}$ , that the behavior is pre-

<sup>1</sup> Miquel: *Ann. chim. phys.*, 1877 [5], **11**, 318.

<sup>2</sup> *Ber. d. chem. Ges.*, **25**, R. 640.

<sup>3</sup> *Loc. cit.*

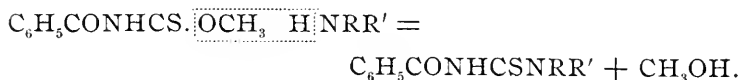
<sup>4</sup> *J. Chem. Soc. (London)*, 1899, 378.

<sup>5</sup> Dritte Auflage, II, p. 1181.

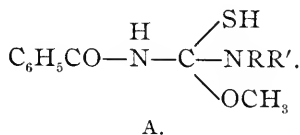
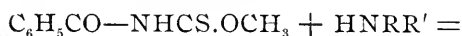
<sup>6</sup> Wheeler and Barnes: *This JOURNAL*, **22**, 141.

<sup>7</sup> *Ibid.*

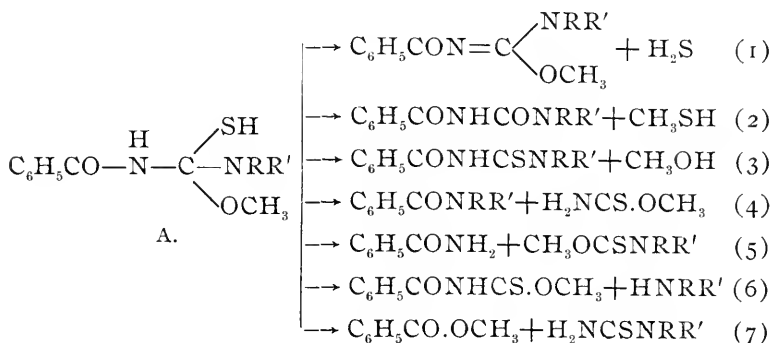
cisely the reverse. These compounds react with ammonia and organic bases at ordinary temperatures, but the course of the reaction is not what might, perhaps, be expected, since a smooth direct replacement, as represented by the following equation, does not take place :



We find, instead of this, that the benzoylthioncarbamic esters unite with 1 molecule of a primary or secondary organic base, giving addition-products, which, we believe, are best represented by the general formula A.



The crude addition-products in most cases appear to be oils or varnishes which decompose more or less readily. We have isolated two examples of these, however, and in one case the product is a solid. An addition-product, as represented here, might be expected to decompose, on warming or on standing, in at least seven different ways, giving the following compounds or their decomposition-products :



As a matter of fact we have obtained examples of the first six of these modes of decomposition. The ease and manner

in which the addition-products decompose depend mostly on the character of the amine radicals R and R', and it may be stated that the above decompositions probably do not all take place in a single experiment. Generally, only two or three of them occur simultaneously. The most widely observed are represented by reactions (1) and (2), while of 13 amines which were allowed to act on benzoylmethyl and ethylthioncarbamate esters, reaction (3) was found to take place in quantity in only one instance.

For example, alcoholic ammonia reacts with ethyl benzoylthioncarbamate almost quantitatively according to (1). The aryl amines, aniline, toluidine, xylydine,  $\alpha$ -naphthylamine, etc., and also benzylamine, react mostly according to (1) and to a less extent as represented by (2). A considerable evolution of hydrogen sulphide takes place (1), while mercaptan (2) is also noticed, and the corresponding benzoyl-arylureas are easily isolated in a state of purity. The presence of benzoylpseudourea ethers (1) was established as shown below.

Diisobutylamine reacts with methyl benzoylthioncarbamate according to (1), (2), (3), and (4). On heating a mixture of these substances, which in the cold forms a varnish, hydrogen sulphide, mercaptan, and alcohol were evolved. The presence of benzoylpseudomethyldiisobutylurea,  $\text{C}_6\text{H}_5\text{CO}-\text{N}=\text{C} \begin{matrix} \text{N}(\text{C}_4\text{H}_9)_2 \\ \text{OCH}_3 \end{matrix}$ , was established and benzoyldiisobutylthiourea and diisobutylbenzamide were isolated.

Ethyl acetylthioncarbamate reacts with aniline, on warming, mostly according to (4), and  $\beta$ -naphthylamine was observed to behave in a similar manner with the benzoylmethyl ester.

Diisoamylamine unites with methyl benzoylthioncarbamate giving an example of the addition-product A, which is a solid at ordinary temperatures. The ester and amine combine, when mixed in molecular proportions, with evolution of heat, but no gas is given off until the addition-product is heated to about  $80^\circ$ , the decomposition then proceeding chiefly according to (5) and (1). Hydrogen sulphide is evolved and benzamide (5) and diamylamine are obtained as the chief



products of the reaction. The same products are obtained when hydrogen sulphide is passed into benzoylpseudomethyl-

diisoamylurea,  $\text{C}_6\text{H}_5\text{CO}-\text{N}=\text{C} \begin{cases} \text{N}(\text{C}_5\text{H}_{11})_2 \\ \text{OCH}_3 \end{cases}$ , at  $60^\circ$ . The fact

that the pseudourea ether is not obtained here, at least not as the chief product, is therefore explained. The presence of diisoamylthiourethane was looked for but it was not found. When this addition-product is allowed to stand over sulphuric acid a slow decomposition or dissociation according to (6) takes place.

The addition-product in the case of diethylamine differs from the above, inasmuch as it is an oil which, on standing, gives benzamide.

Although in every case more or less hydrogen sulphide was evolved in the action of amines on the acylthioncarbamic esters, thus indicating the formation of acylpseudourea ethers, nevertheless these interesting compounds could not be isolated from the other by-products in these reactions (except in the case of ammonia). They form oils which cannot be distilled out of the mixture, without decomposition, even under reduced pressure. Their presence was established, however, not only by the fact that hydrogen sulphide was evolved, but also by the comparison of the properties of the reaction-products with those of the corresponding acylpseudourea ethers. We prepared the latter from the benzoylimidothiocarbonic

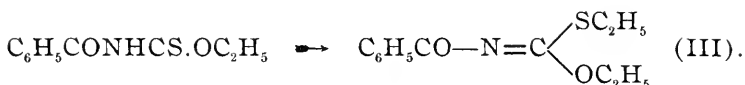
esters,  $\text{C}_6\text{H}_5\text{CO}-\text{N}=\text{C} \begin{cases} \text{SR} \\ \text{OR} \end{cases}$ , and it was found that the action

of dilute hydrochloric acid affords a delicate test for their presence (see below).

The benzoylimidothiocarbonic esters are readily formed by the action of alkyl iodides on the sodium or potassium salts of the benzoylthioncarbamic esters,<sup>1</sup> in the same manner, as it has been found in general that the derivatives of the thioncarbamic esters react in the pseudoform, giving the substituted imidothiocarbonic esters:<sup>2</sup>

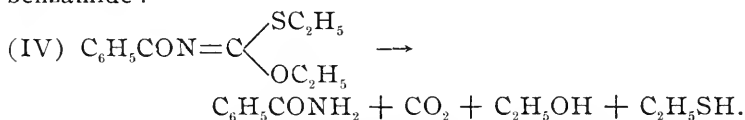
<sup>1</sup> Lössner: J. prakt. Chem., 1874 [2], 10, 237; Dixon: J. Chem. Soc. (London), 1899, 380.

<sup>2</sup> Liebermann: Ann. Chem. (Liebig), 270; Busch and Lingenbrink: Ber. d. chem. Ges., 32, 2620; Fromm and Block: *Ibid.*, 2212; and Wheeler and Barnes: This JOURNAL, 24, 60.

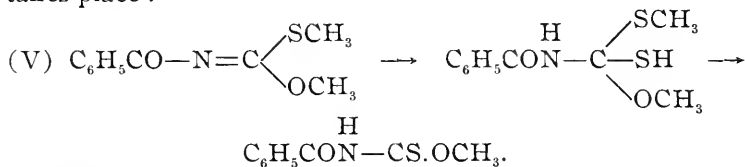


Hitherto only one compound of this series has been isolated. Lössner obtained diethyl benzoylimidothiocarbonate (III) in the above manner. He states that it is an oil which decomposes at  $44^\circ$ , giving off mercaptan; while at higher temperatures benzonitrile and a syrupy residue are obtained. He assigned the incorrect formula,  $\text{C}_6\text{H}_5\text{CON}(\text{C}_2\text{H}_5)\text{CO}.\text{SC}_2\text{H}_5$ , to this substance, and the solid obtained by treating this with ammonia was regarded as benzoylethylurea. Dixon,<sup>1</sup> however, has shown that this is really a pseudourea.

The benzoylimidothiocarbonic esters, when prepared as described below, are oils without exception, which, as far as we have observed, distil unaltered under reduced pressure. For example, the oil of Lössner, when pure, has an odor like the xanthic esters, and it boils at about  $210^\circ$  at 19 mm. pressure, without the slightest sign of decomposition. The reaction which affords these oils is so smooth that for most purposes it is unnecessary to distil them. In some of our experiments the ether solutions of the crude products, after washing, were thoroughly dried over calcium chloride and then evaporated in a vacuum at  $100^\circ$ . Under these conditions the only impurity that appears to be present is benzamide, and then, if heating has been avoided before drying, only in very small quantities. When the oils are heated with water they give benzamide :<sup>2</sup>



We find that with hydrogen sulphide at  $100^\circ$  the following takes place :

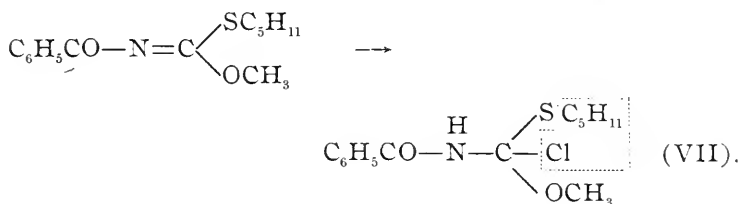
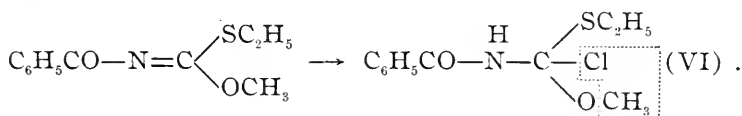


<sup>1</sup> *Loc. cit.*

<sup>2</sup> Lössner : *Loc. cit.*

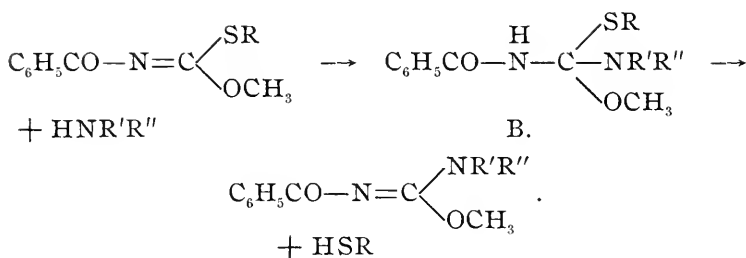
The ester is converted into benzoylthioncarbamic ester with loss of mercaptan.

That the oils obtained in the above manner are homogeneous is shown in each case by their smooth reactions with hydrogen chloride and with organic bases. We have obtained instances of the two following decompositions when the oils are dissolved in benzene and treated at ordinary temperatures with dry hydrogen chloride :



The decomposition with hydrogen chloride proceeds, with the series  $\text{C}_6\text{H}_5\text{CO}-\text{N}=\text{C} \begin{array}{l} \text{SAlk} \\ \text{OCH}_3 \end{array}$  chiefly or entirely, according to reaction (VI), giving benzoylthiolcarbamic esters. When the alkyl group is amyl it separates according to reaction (VII).

When the benzoylimidothiocarbonic esters are treated with organic bases they readily react, giving off mercaptan and forming acylpseudourea ethers. The reaction is, in all probability, perfectly analogous to that of the above-mentioned benzoylthioncarbamic esters, except that the intermediate addition-product B (below) decomposes more smoothly and not in such a variety of ways as found in the case of the addition-product A. In most cases the reaction appears to take place quantitatively, as follows :



It appears that previously this action has only been investigated with ammonia, Dixon having shown that methyl- and ethyl- $\psi$ -n-benzoylurea are formed in this way. He obtained these acylpseudourea ethers as crystalline compounds melting from  $74^\circ$ - $75^\circ$  and  $77^\circ$ - $78^\circ$ , respectively.

The compounds of this type which we have obtained with organic bases are oils. Those which we attempted to distil decomposed. They appear to be even more reactive than the interesting series of pseudourea ethers first obtained by Lengfeld and Stieglitz,<sup>1</sup> which have been so thoroughly studied by Stieglitz and Dains.<sup>2</sup> In properties they are closely similar to the acylimido esters<sup>3</sup> and acylamidines,<sup>4</sup> to both of which series the compounds belong, since they have the structure of both these classes combined. We find that the most striking reaction, at present, of this series of benzoylpseudourea ethers is the ease with which they act with hydrochloric acid. Most of the pseudourea ethers mentioned above, as well as those described by Stieglitz and McKee,<sup>5</sup> give salts with hydrochloric acid from which platinum double salts can be prepared. In stability, they approach the salts of the imido ethers prepared by Pinner and others. We observed similar properties among the benzoylpseudourea ethers in the case of those prepared with ammonia. For example, benzoyl-

pseudoethylurea,  $\text{C}_6\text{H}_5\text{CO}-\text{N}=\text{C} \begin{array}{l} \nearrow \text{NH} \\ \searrow \text{OC}_2\text{H}_5 \end{array}$ , dissolves in cold

<sup>1</sup> Ber. d. chem. Ges. (1894), **27**, 926.

<sup>2</sup> J. Am. Chem. Soc., **21**, 136.

<sup>3</sup> Wheeler and Walden: *This Journal*, **19**, 129; Wheeler, Walden, and Metcalf: *Ibid.*, **20**, 64; and **19**, 217.

<sup>4</sup> Wheeler and Walden: *Ibid.*, **20**, 569.

<sup>5</sup> Ber. d. chem. Ges., **33**, 807.

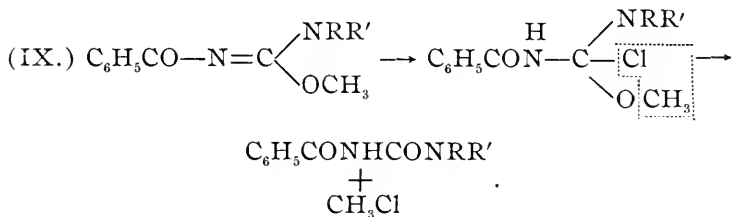
hydrochloric acid, and gold chloride gives a bright-yellow precipitate of fine needles. A gold determination in this agreed

with the formula,  $\text{C}_6\text{H}_5\text{CO}-\text{N}=\text{C} \begin{matrix} \text{NH}_2 \\ \text{OC}_2\text{H}_5 \end{matrix} \cdot \text{HCl} \cdot \text{AuCl}_3$ . This salt is quite stable and it melts with decomposition at about  $140^\circ$ .

When, on the other hand, the more negative benzoylpseudo-urea ethers, especially those containing aryl groups, are treated with cold, aqueous hydrochloric acid, a reaction starts immediately. The solutions effervesce, alkyl chloride being driven off, whereupon, as a rule, the oils are quantitatively converted into beautifully crystallizable colorless acylureas. In the case of the aryl derivatives the oils crystallize immediately, while the aliphyl compounds solidify more slowly.

This is in striking contrast to some of the pseudourea ethers of Stieglitz and Dains which are not completely decomposed by cold aqueous hydrochloric acid after a month's standing.

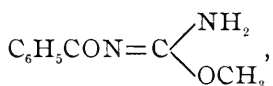
The following represents the course of the reaction with hydrochloric acid :



This sensitiveness to hydrochloric acid finds a perfect parallel in the deportment of the acylimido esters, and it is shared also to a less extent by the acylamidines. The results show that the more negative the character of the radical in the imido ester grouping,  $\text{RN}=\text{CR}'\cdot\text{OR}''$ , the more sensitive are the compounds in regard to decomposition by hydrogen chloride, a fact also noticed by Stieglitz and Dains in other cases.

In this connection it is interesting to note that pure water has little tendency to react with most of the benzoylpseudo-

urea ethers. This is well illustrated by the fact that Dixon, in showing the structure of the acylpseudourea ether,

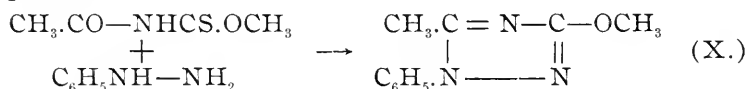


heated the compound in closed tubes with ten parts water from  $105^\circ$ – $125^\circ$  "without any sign of change. On raising the temperature to  $150^\circ$ – $160^\circ$  action occurred, carbonic anhydride escaped on opening the tube, the liquid contents of which smelt of ammonia and methyl benzoate." In other words, the material refused to react with water without total decomposition.

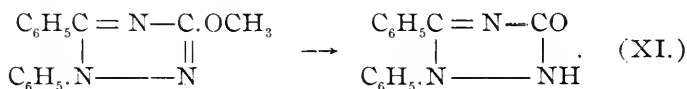
On the other hand, we find that if this compound which melts at  $77^\circ$  is gently warmed with water, in the presence of hydrochloric acid, it fuses, but in a few moments it solidifies, whereupon the material is quantitatively converted into benzoylurea,  $\text{C}_6\text{H}_5\text{CONHCONH}_2$ , melting at  $214^\circ$ . The above procedure affords a smooth method for the preparation of most of the  $\alpha$ - $\beta$ -benzoylureas since the different steps of the process give almost quantitative yields.

We hope later to describe other reactions of the acylpseudourea ethers.

The acylthioncarbamic esters react with phenylhydrazine, giving off hydrogen sulphide in the cold. The products, however, are not pseudourea or pseudosemicarbazidic esters, as might be expected, but the following ring-formed compounds:



That the products are alkyloxytriazoles is shown by the behavior of the compound from methyl benzoylthioncarbamate. This, when boiled with hydrochloric acid, slowly gives up the methyl group and the so-called 1,5-diphenyl-3-oxytriazole (1,5-diphenyl-3-triazolone?) is obtained:



The product (XI.) is identical with that obtained by Young<sup>1</sup> from phenylsemicarbazide and benzaldehyde, and by Widman<sup>2</sup> from benzoylsemicarbazide by treating with alkali.

Phenylhydrazine, therefore, reacts with the thionacylurethanes in a different manner than with the ordinary acylurethanes, inasmuch as Andreocci<sup>3</sup> found that acetylurethane gives 1-phenyl-3-methyl-5-triazolone, while the above reactions lead to the formation of the isomeric compound, 1-phenyl-5-methyl-3-triazolone.

#### EXPERIMENTAL PART.

##### *The Action of Acylthioncarbamic Esters with Organic Halides.*

##### *Preparation of Methyl Acetylthioncarbamate,*

$\text{CH}_3\text{CO}-\text{NHCS}.\text{OCH}_3$ .—In our first experiments we boiled acetyl chloride in benzene solution with an excess of lead sulphocyanide for several hours; methyl alcohol was then added, in slight excess, and the mixture boiled for about thirty minutes. On evaporating, an oil was obtained, which, on cooling, solidified. It was crystallized from petroleum ether, when it separated in arborescent crystals melting at  $79^\circ$ – $80^\circ$ . It is readily soluble in water, alcohol, benzene, and chloroform, and when boiled with freshly precipitated mercuric oxide, it is desulphurized. A nitrogen determination gave:

	Calculated for $\text{C}_4\text{H}_7\text{NO}_2\text{S}$ .	Found.
N	10.52	10.12

This compound is more easily obtained by warming methyl thioncarbamate with acetic anhydride on the water-bath. We found later that it is unnecessary to use lead sulphocyanide for the preparation of either acetyl or benzoyl rhodanide. In order to obtain a good yield of acetyl rhodanide, acetyl chloride is boiled with an excess of finely pulverized potassium sulphocyanide, in the presence of a little toluene, and under a pressure of about 900 mm. of mercury. In the case of benzoyl rhodanide, an increase in pressure is unnecessary, for example: 15 grams of benzoyl chloride were

<sup>1</sup> Ber. d. chem. Ges., 29, 2311.

<sup>2</sup> Ibid., 29, 1951.

<sup>3</sup> Ibid., 22, R. 737.

boiled with 10.5 grams of potassium sulphocyanide in 10 cc. of toluene for fifteen minutes and then the material was distilled at 36–35 mm. pressure, when, below  $90^{\circ}$ , the toluene was collected; from  $142^{\circ}$ – $151^{\circ}$  only a few drops distilled over; and then from  $151^{\circ}$ – $151.5^{\circ}$  the entire remainder was obtained except an insignificant colored residue. The last fraction consisted of practically pure rhodanide.

*Methyl Acetylthiolcarbamate*,  $\text{CH}_3\text{CO}-\text{NHCO}\cdot\text{SCH}_3$ .—We observed the formation of this compound when 4 grams of methyl acetylthioncarbamate were allowed to stand with one molecular proportion of methyl iodide, in a sealed tube at  $40^{\circ}$ – $45^{\circ}$ , for three weeks. The material when crystallized from benzene, separated in the form of fine needles, melting from  $145.5^{\circ}$ – $146^{\circ}$ . It is insoluble in cold water, but readily soluble in hot water and in alcohol. It was not desulphurized when boiled with mercuric oxide, and a nitrogen determination gave:

	Calculated for $\text{C}_4\text{H}_7\text{NO}_2\text{S}$ .	Found.
N	10.52	10.15

When methyl acetylthioncarbamate was heated with an excess of methyl iodide on the steam-bath for from six to seven hours no molecular rearrangement occurred, and no change was noticed when the mixture was allowed to stand at ordinary temperature for three weeks. That a rearrangement had taken place in the first experiment was shown by the fact that the compound melting at  $145.5^{\circ}$ – $146^{\circ}$  can also be prepared by warming methyl thiolcarbamate with acetic anhydride on the water-bath.

*Ethyl Acetylthioncarbamate*,  $\text{CH}_3\text{CO}-\text{NHCS}\cdot\text{OC}_2\text{H}_5$ , was prepared like the methyl ester. Dixon<sup>1</sup> has shown that when pure acetyl rhodanide is mixed with alcohol a violent reaction takes place, fused sulphur and other products being obtained. However, this ester can be prepared from the rhodanide if the latter is mixed with benzene. It is difficultly soluble in water, but readily soluble in alcohol and benzene. From water it crystallizes in prisms and melts from  $100^{\circ}$ – $101^{\circ}$ . A nitrogen determination gave:

<sup>1</sup> J. Chem. Soc. (London), 61, 529.



	Calculated for $C_6H_9NO_2S$ .	Found.
N	9.5	9.9

Attempts to arrange this thion ester into the isomeric thiol compound were without success. When heated with ethyl iodide in a closed tube to  $100^\circ$ , ammonium iodide was obtained as the only solid product. When heated from  $80^\circ$ – $90^\circ$  a product was obtained crystallizing in plates and melting at  $105^\circ$ – $106^\circ$ , and otherwise having all the properties of ethyl thiolcarbamate,  $H_2NCO.SC_2H_5$ . When allowed to stand dissolved in ethyl iodide for four months, no action was observed. This is in marked contrast with the ease with which xanthogenamide and ethyl thionphenylcarbazinate undergo a molecular rearrangement.

*Methyl Benzoylthioncarbamate*,  $C_6H_5CO-NHCS.OCH_3$ .—This and the following ethyl ester were prepared by boiling benzoyl chloride, diluted with a little toluene, with an excess of potassium sulphocyanide. For 100 grams of benzoyl chloride the reaction was practically complete in a few hours; then, on cooling, alcohol was added and warmed for a short time. The toluene was then removed in a current of steam and the residue crystallized from dilute alcohol, when the ester separated in needles melting at  $97^\circ$ , as stated by Miquel.<sup>1</sup>

*Methyl Benzoylthiolcarbamate*,  $C_6H_5CO-NHCO.SCH_3$ .—This compound was obtained when 8 grams of the above ester were heated with methyl iodide in a closed tube from  $80^\circ$ – $90^\circ$  for six hours. On opening the tube it was found to be filled with a mass of beautiful, long prisms, some of them from 1–2 inches in length. On crystallizing these from alcohol they melted from  $152^\circ$ – $153^\circ$ , and a nitrogen determination gave :

	Calculated for $C_6H_9NO_2S$ .	Found.
N	7.1	6.9

This thiol ester is soluble in alkali and is precipitated unaltered by acids. When boiled with mercuric oxide it gave no precipitate of mercuric sulphide, thus differing from the thion ester.

<sup>1</sup> *Loc. cit.*

When the thion ester was heated with methyl iodide to  $100^{\circ}$ – $110^{\circ}$  decomposition took place, and a compound free from sulphur and difficultly soluble in alcohol was obtained. It was insoluble in hot water and sodium hydroxide, and it separated from alcohol in small needles, melting at about  $215^{\circ}$  with effervescence. It crystallizes unaltered from nitric acid, and a nitrogen determination gave 11.1 per cent. It was not identified.

*Ethyl Benzoylthioncarbamate*,  $C_6H_5CO-NHCS.OC_2H_5$ .—This compound was first obtained by Lössner,<sup>1</sup> the structure  $C_6H_5CO \begin{array}{c} \diagup \\ \diagdown \end{array} NCO.SH$  being assigned to it, while in Beilstein's "Handbuch" it is represented by the formula



Its correct formula, the thion structure, was given to it by Miquel<sup>1</sup> and further confirmed by Dixon.<sup>1</sup> For our use we prepared it from the rhodanide as above stated. It forms colorless needles from dilute alcohol and it melts from  $73^{\circ}$ – $74^{\circ}$ . It is desulphurized by boiling with mercuric oxide, and it has little if any tendency to undergo a molecular rearrangement with ethyl iodide. It was not changed by standing for two weeks with ethyl iodide or by heating it from  $95^{\circ}$ – $100^{\circ}$  or from  $100^{\circ}$ – $110^{\circ}$ . When heated with the iodide from  $125^{\circ}$ – $130^{\circ}$  for four hours benzamide was obtained.

*Benzoylcarbaminthioglycollic Acid*,  $C_6H_5CONHCO.SCH_2COOH$ .—When molecular quantities of methyl benzoylthioncarbamate and chloracetic acid were heated for eight hours on the steam-bath, a slow effervescence took place. The product then crystallized from dilute alcohol gave colorless needles melting from  $169^{\circ}$ – $170^{\circ}$ . This material was not desulphurized by boiling with mercuric oxide. It is soluble with difficulty in benzene, and a nitrogen determination gave :

	Calculated for $C_{10}H_9NO_4S$ .	Found.
N	5.8	6.1

<sup>1</sup> Loc. cit.

*Benzoylurea*,  $C_6H_5CO-NHCONH_2$ .—On treating the above compound, dissolved in alcohol, with ammonia, a mass of small lozenge-shaped plates separated. This material was free from sulphur and melted from  $214^\circ-215^\circ$  with slight effervescence. It was soluble in hot water and in sodium hydrate and was precipitated from the latter solution unaltered by hydrochloric acid. A nitrogen determination gave :

	Calculated for $C_8H_8N_2O_2$ .	Found.
N	17.0	16.7

It was stated by Zinin,<sup>1</sup> who first obtained benzoylurea, that this compound melts "gegen  $200^\circ$ ". Geuther, Scheitz, and Marsh<sup>2</sup> give  $208^\circ$ . That these melting-points are too low is shown by the above ; moreover, we have obtained benzoylurea by other methods and in each case it was found to melt at  $214^\circ-215^\circ$ .

*Methyl Dibenzoylthioncarbamate*,  $(C_6H_5CO)_2NCS.OCH_3$ .—The sodium salt of methyl benzoylthioncarbamate was prepared by dissolving the ester in methyl alcohol, adding a strong solution of sodium methylate, and then precipitating with ether. Thus prepared it forms a sandy powder which was dried over sulphuric acid in a vacuum. On treating this, suspended in benzene, with the calculated quantity of benzoic anhydride, and boiling for six hours, an oil was obtained which solidified on cooling. On crystallizing this from petroleum ether, colorless plates separated which melted, when pure, from  $81^\circ-82^\circ$ , and a nitrogen determination gave the following result :

	Calculated for $C_{16}H_{13}NO_3S$ .	Found.
N	4.6	4.7

When this diacylthiourethane was treated with a molecular proportion of phenylhydrazine in the cold, hydrogen sulphide was evolved and, on crystallizing the product from benzene, needles or prisms were obtained melting from  $166^\circ-167^\circ$ , which proved to be benzoylphenylhydrazine.

When the sodium salt of methyl benzoylthioncarbamate

<sup>1</sup> Ann. Chem. (Liebig), 92, 404.

<sup>2</sup> Ztschr. Chem., 1868, 305.

was treated in dry benzene with acetic anhydride, and the product crystallized from dilute alcohol, nothing but unaltered ester was obtained.

*Methylene Thiolcarbamate*,  $\text{H}_2\text{NCO.SCH}_2\text{S.CONH}_2$ .—Gabriel and Heyman<sup>1</sup> found that ethylene bromide and thioamides give thiazoline derivatives, while Pinkus<sup>2</sup> obtained from trimethylene chlorobromide and thioamides the so-called pen-thiazolines. In the case of xanthogenamide, he found that the reaction gave a compound or mixture agreeing with the formula,  $\text{C}_4\text{H}_8\text{NOS} \frac{\text{Br} + \text{Cl}}{2}$ . Recently Busch<sup>3</sup> has found that the potassium salts of the dithiocarbazinic esters give ring-formed compounds with ethylene bromide, diazthins, and not the ethylene esters. In a recent paper Wheeler and Barnes<sup>4</sup> have described the action of ethylene bromide on xanthogenamide. They obtained a product which appeared to be the ethylene ester of thiolcarbamic acid. It therefore seemed of interest to determine whether other alkyl dihalides also act abnormally with xanthogenamide. For this purpose we warmed methylene iodide with xanthogenamide in molecular proportions for five hours on the steam-bath, when the odor of the iodide disappeared. On cooling and crystallizing from water, small compact crystals were obtained, melting from  $168^\circ$ – $170^\circ$ , which, on analysis, gave the following result :

	Calculated for $\text{C}_3\text{H}_6\text{O}_2\text{N}_2\text{S}_2$ .	Found.
N	16.8	16.3

*Ethylene Thiolcarbamate*,  $\text{H}_2\text{NCO.SCH}_2\text{—CH}_2\text{S.CONH}_2$ , from ethylene bromide and xanthogenamide, has already been described,<sup>5</sup> but the melting-point was omitted ; it melts from  $231^\circ$ – $232^\circ$ .

*Trimethylene Thiolcarbamate*,  $\text{H}_2\text{NCO.SCH}_2\text{CH}_2\text{CH}_2\text{S.CO NH}_2$ , from trimethylene bromide and xanthogenamide, after two hours' heating on the water-bath, crystallizes from hot water in plates, and melts from  $177^\circ$ – $179^\circ$ . It is extremely soluble

<sup>1</sup> Ber. d. chem. Ges., **23**, 157 ; **24**, 783.

<sup>2</sup> *Ibid.*, **26**, 1083.

<sup>3</sup> J. prakt. Chem., **60**, 26.

<sup>4</sup> This JOURNAL, **22**, 151.

<sup>5</sup> Wheeler and Barnes : *Loc. cit.*

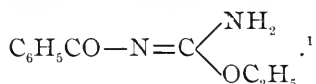
in alcohol and difficultly soluble in benzene. A nitrogen determination gave:

	Calculated for $C_6H_{10}O_2N_2S_2$ .	Found.
N	14.4	14.1

When *isobutylene bromide* and xanthogenamide were heated on the water-bath for five hours cyanuric acid, ethyl thiolcarbamate, and unaltered material were obtained.

*The Behavior of Acylthioncarbamic Esters with Ammonia and Amines.*

*Ethyl Benzoylthioncarbamate and Ammonia.*—Five grams of the ester were dissolved in an excess of alcoholic ammonia and the solution allowed to stand at rest for three days. The action began immediately, and hydrogen sulphide was slowly evolved at ordinary temperatures. After the action was complete the alcohol was distilled off, and the first portions were tested for mercaptan, but with a negative result. When most of the alcohol had evaporated, the remaining solution was poured into dilute potassium hydrate, when an oil separated which soon solidified. On crystallizing this from petroleum ether, beautiful, long, needle-like prisms separated, which melted sharply from  $74^{\circ}$ – $75^{\circ}$ . This compound has practically the same melting-point as ethyl benzoylthioncarbamate; that it was not this substance was shown by mixing the two, when the mixture melted at  $45^{\circ}$ . The properties of the substance show that it is identical with the compound first obtained by Lössner, which Dixon has shown has the formula,



In other words, it is *benzoylpseudoethylurea*. The reaction appears to be practically quantitative. When this substance is treated with dilute hydrochloric acid it dissolves, and on gently warming the solution and again cooling *benzoylurea*, melting from  $214^{\circ}$ – $215^{\circ}$ , separates.

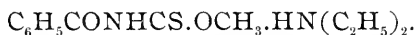
*Benzoylpseudoethylurea Chloraurate*,  $C_6H_5CO-N=C(NH_2).OC_2H_5.HCl.AuCl_3$ , is precipitated from the above hydrochloric

<sup>1</sup> *Loc. cit.*

acid solution on the addition of gold chloride. It forms fine, bright-yellow needles, which are difficultly soluble in water and melt at about  $140^{\circ}$ . A gold determination gave :

	Calculated for $C_{10}H_{13}N_2O_2Cl_4Au.$	Found.
Au	37.0	37.1

*Methyl Benzoylthioncarbamate and Diethylamine* unite at ordinary temperature, without evolution of gas, to form a varnish which refused to solidify on cooling or on keeping in a vacuum desiccator over sulphuric acid for two to three days. At the end of this time free amine appeared to be absent and a nitrogen determination gave 9.89 per cent nitrogen instead of 10.49, which is required for

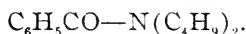


The result is, perhaps, as close as could be expected, considering the fact that the material does not permit of a better method of purification. The material, on standing for three weeks in a desiccator, deposited benzamide. On heating, the result was the same; hydrogen sulphide and other products were given off, and only a small amount of oil besides benzamide was obtained. It dissolves very readily in alcohol and benzene, and is precipitated as an oil by petroleum ether.

*Ethyl Benzoylthioncarbamate and Diisobutylamine* combine to form a varnish as in the previous case. When 16 grams of the ether were heated with 10 grams of the amine, reaction began at about  $80^{\circ}$  and 600 cc. of hydrogen sulphide were collected over water, and the presence of alcohol and mercaptan was also identified in the volatile products. On cooling, a thick oil was obtained which, when treated with hydrochloric acid, gave off ethyl chloride and solidified completely. On crystallizing then from strong alcohol, colorless prisms separated which occurred in twins, in the form of beautiful crosses, and melted at  $130^{\circ}$ – $132^{\circ}$ . This material was found to contain sulphur, and a nitrogen determination agreed with the calculated for *benzoyldiisobutylthiourea*,  $C_6H_5CONHCSN(C_4H_9)_2$ .

	Calculated for $C_{16}H_{25}N_2OS.$	Found.
N	9.59	9.95

A portion of the above product, which had not been treated with hydrochloric acid, was distilled at 25 mm. pressure, when, after decomposition of some constituent (the pseudo-urea ether (?)), a considerable portion of oil distilled over between 182°–190°. This was redistilled at ordinary pressure when it boiled mostly from 288°–311°; it was then treated with alkali and the insoluble part was extracted with ether, whereupon, on evaporating, a brilliant mass of stout prisms separated. This compound was purified by crystallizing from petroleum ether. It melted at 65°, and a nitrogen determination agreed with the calculated for *diisobutylbenzamide*:



	Calculated for $\text{C}_{16}\text{H}_{23}\text{NO}$ .	Found.
N	6.0	6.4

The alkaline solution on acidifying gave benzoyldiisobutylthiourea. Diisobutylbenzamide, like its homologues, is very soluble in most organic solvents, from which solutions it is obtained as an oil which solidifies to form beautiful crystals.

*Methyl Benzoylthioncarbamate and Diisoamylamine* combine with a decided evolution of heat, to form an oil which quickly solidifies. No trace of mercaptan or hydrogen sulphide is given off at ordinary temperatures and, when this addition-product is prepared by mixing molecular quantities, it melts at 55°–60°. It is extremely soluble in benzene and alcohol, and apparently undergoes dissociation, since petroleum ether precipitates unaltered methyl benzoylthioncarbamate. On standing in a desiccator over sulphuric acid, it slowly decomposed, becoming oily (separation of free amine), when after a week unaltered ester was obtained. As it could not be purified by crystallization, a portion was prepared by mixing 5 grams of the ester with about 4 grams of diamylamine and grinding the material together in a mortar, after which it was thoroughly pressed on paper and allowed to stand exposed to the air for a short time. A nitrogen determination then gave 8.6 per cent of nitrogen while the calculated for



is 7.9 per cent ; the calculated for unaltered ester being 7.1 per cent.

When the addition-product was heated, evolution of hydrogen sulphide and mercaptan were noticed at its melting-point, and, on maintaining the temperature at about 80°, an oil was obtained which, when treated with benzene, deposited plates. These were crystallized from water, whereupon they melted from 126°–127°; they were free from sulphur, and a nitrogen determination gave results agreeing with the calculated for *benzamide*.

	Calculated for $C_7H_7NO$ .	Found.
N	11.5	11.2

An attempt was made to isolate the pseudourea ether that is formed here, which constitutes the oil removed by benzene in the above experiment. With this object we tried distilling the addition-product at 15 mm. pressure ; on heating, the pressure rose to 40 mm., and up to 200° an oil and a solid distilled over. The oil consisted mostly of benzonitrile and the solid was benzamide. When this pseudourea ether is treated with cold hydrochloric acid, methyl chloride is evolved and benzamide and diamylamine hydrochloride are obtained. The formation of benzoyldiisoamylurea was not observed.

*Ethyl Benzoylthioncarbamate and Benzylamine* energetically react with evolution of heat, hydrogen sulphide and mercaptan are apparently evolved, and the mixture readily solidifies. On crystallizing then from 95 per cent alcohol, flattened prisms separate which melt sharply at 89°. The material does not contain sulphur, and a nitrogen determination agrees with the calculated for *benzoylbenzylurea*,



	Calculated for $C_{15}H_{14}N_2O_2$ .	Found.
N	11.0	10.7

*Ethyl Benzoylthioncarbamate and Aniline*.—Ten grams of the former were mixed with one molecular proportion of the latter and the mixture was warmed for from eight to nine hours on the steam-bath, when hydrogen sulphide ceased being



evolved and an oil was obtained. On standing, crystals separated which formed an arborescent mass from dilute alcohol, and melted from  $202^{\circ}$ – $203^{\circ}$ . This material was free from sulphur, and a nitrogen determination gave the following result :

	Calculated for $C_{14}H_{12}N_2O_3$ .	Found.
N	11.66	11.68

This material agrees in properties with *benzoylphenylurea*,  $C_6H_5CONHCONHC_6H_5$ , which Blacher<sup>1</sup> has prepared by another method. He gives its melting-point as  $204^{\circ}$ – $205^{\circ}$ . This compound has also been obtained by Kuhn,<sup>2</sup> who states that it melts at  $199^{\circ}$ , and also by Beckmann and Köster, who give  $204^{\circ}$  as its melting-point.

*Ethyl Benzoylthioncarbamate and Paratoluidine*.—A mixture of these substances in molecular proportions were heated for from seven to eight hours on the steam-bath. Hydrogen sulphide was given off during the reaction; the product thus contained consisted chiefly of pseudoethylparatolylbenzoylurea,  $C_6H_5CON \equiv C(OC_2H_5) - NHC_6H_4CH_3$ , and was an oil which on exposure to the laboratory atmosphere deposited crystals after two days. On pressing these on a plate and crystallizing from dilute alcohol, small narrow prisms were obtained which melted from  $80^{\circ}$ – $81^{\circ}$ . These were free from sulphur, and a nitrogen determination showed that this material was *benzoylparatolylurea*,  $C_6H_5CO - NHCONHC_6H_4CH_3$ .

	Calculated for $C_{15}H_{14}N_2O_2$ .	Found.
N	11.0	10.7

In order to show the presence of pseudoethylparatolylurea, 3 grams of methyl benzoylcarbamate and 1.6 grams of toluidine were heated together; a lively effervescence of hydrogen sulphide took place at  $90^{\circ}$ , and in about one hour, with these quantities, it practically ceased. The oil thus obtained was treated with 10 cc. of about 20 per cent hydrochloric acid, and the gas which was evolved was collected over water, in which it was partly soluble. In one hour over 80 cc. of methyl chlo-

<sup>1</sup> Ber. d. chem. Ges., **28**, 435.

<sup>2</sup> *Ibid.*, **17**, 2881.

<sup>3</sup> Ann. Chem. (Liebig), **274**, 28.

ride were obtained. When methyl benzoylthioncarbamate was treated with hydrochloric acid under the same conditions, no gas was evolved. On warming, however, methyl chloride is evolved.

With the object of isolating the pseudourea ether that is formed in this reaction, we subjected the reaction-product to distillation, starting at 13 mm. pressure. At 165° the pressure rose, and up to 200°, at 20 mm. pressure, a portion had distilled over; in this we identified benzamide and benzonitrile, which showed that the material had decomposed.

When ethyl acetylthioncarbamate was warmed with *p*-toluidine, hydrogen sulphide was evolved, and an oil and a solid were obtained; on crystallizing the solid from alcohol, it melted at 147° and had all the properties of paracetoluide. The oil was not examined.

*Ethyl Benzoylthioncarbamate and 2,4-Dimethylaniline* were heated together in molecular proportions on the water-bath, and an attempt was made to collect the mercaptan given off, but it was carried off in the stream of hydrogen sulphide which escaped. On cooling, an oil was obtained together with some solid. The solid was filtered off and, on crystallizing from alcohol, it melted from 215°–217°. On treating the oil with hydrochloric acid, ethyl chloride was evolved and the material solidified when, on crystallizing from alcohol, it likewise melted from 215°–217°. A nitrogen determination gave :

	Calculated for $C_{16}H_{16}N_2O_2$ .	Found.
N	10.4	10.5

This compound is therefore  $\alpha, \beta$ -benzoylmetaxylylurea,



*Ethyl Benzoylthioncarbamate and p-Anisidine* reacted at once with a rapid evolution of hydrogen sulphide. When warmed on the water-bath until this ceased, and then cooled, very little oil was obtained. The chief quantity of the reaction-product was solid. From this, two compounds were separated by means of alcohol and benzene. The more soluble one, the chief product, proved to be benzoylparaanisidine. Boiling the product with alcohol gave a mass of colorless prisms

which melted from  $216^{\circ}$ – $218^{\circ}$ , and a nitrogen determination of this substance, which burns slowly, gave the following result :

	Calculated for $C_{15}H_{14}N_2O_2$ .	Found.
N	10.3	9.8

This material is therefore *benzoylparamethoxyphenylurea*,



When the above oil was treated with hydrochloric acid, it gave off ethyl chloride, showing the presence of benzoyl-pseudoethylparamethoxyphenylurea.

*Methyl Benzoylthioncarbamate and  $\alpha$ -Naphthylamine.*—On warming molecular quantities of these substances until hydrogen sulphide ceased coming off, an oil was obtained which, treated with benzene and petroleum ether, gave a precipitate. When this was boiled with alcohol a residue of cyanphenine, melting at  $230^{\circ}$ , remained. On adding water to the alcoholic solution, and then crystallizing from dilute alcohol, we obtained colorless prisms melting from  $165^{\circ}$ – $166^{\circ}$ . This material contained no sulphur. That it was not benzoyl- $\alpha$ -naphthalide, which melts at  $160^{\circ}$ – $162^{\circ}$ , was shown on mixing these substances, when the mixture melted at  $140^{\circ}$ . A nitrogen determination agreed with the calculated for *benzoyl- $\alpha$ -naphthylurea*,  $C_6H_5CONHCONHC_{10}H_7$ .

	Calculated for $C_{18}H_{14}N_2O_2$ .	Found.
N	9.6	9.8

*Methyl Benzoylthioncarbamate and  $\beta$ -Naphthylamine* gave off hydrogen sulphide on warming, thus showing the formation of a pseudourea ether. The product was obtained as an oil that deposited nothing solid on standing a week. On adding petroleum ether and crystallizing from dilute alcohol, small needles separated which melted at  $156^{\circ}$ . The material contained no sulphur, and a nitrogen determination gave results agreeing with the calculated for *benzoyl- $\beta$ -naphthalide*.

	Calculated for $C_6H_5CONHCONHC_{10}H_7$ .	Calculated for $C_6H_5CONHC_{10}H_7$ .	Found.
N	9.65	5.46	5.26

*Ethyl Benzoylthioncarbamate and Diphenylamine* react with

difficulty and hydrogen sulphide is given off. After heating for three days on the steam-bath an oil was obtained which, when treated with hydrochloric acid, decomposed with the separation of diphenylamine.

*Ethyl Benzoylthioncarbamate and Orthophenylenediamine* were mixed in the proportion of 2 molecules of the former to 1 of the latter in ether solution, when, on evaporating, hydrogen sulphide was given off and a solid was directly obtained. There appeared to be little or no oil in this case. The material, when crystallized from alcohol, separated in lozenge-shaped crystals, which were free from sulphur; they melted at  $235^{\circ}$ , and a nitrogen determination agreed with the calculated for *dibenzoylphenylen diurea*,



	Calculated for $\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}_4$ .	Found.
N	13.9	14.2

*Methyl Benzoylthioncarbamate and Phenylhydrazine*.—When phenylhydrazine is added to the ester, the mixture becomes warm and hydrogen sulphide is given off. On heating, to complete the action, and then cooling, an oil is obtained which readily solidifies. On crystallizing this from dilute alcohol, colorless needles are obtained melting from  $85^{\circ}$ – $86^{\circ}$ . A nitrogen determination agreed with the calculated for *1,5-diphenyl-3-ethoxytriazole*. This material was free from sulphur.

	Calculated for $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}$ .	Found.
N	16.7	16.9

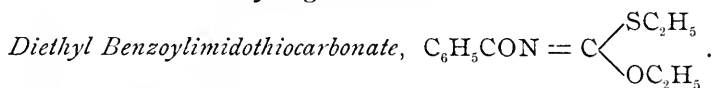
*1,5-Diphenyl-3-triazolone* was obtained when the above was boiled with concentrated hydrochloric acid in alcoholic solution for from eight to nine hours.

*Ethyl Acetylthioncarbamate and Phenylhydrazine* reacted in the cold, giving off hydrogen sulphide, but on standing two weeks nothing solid separated. The material was then distilled at 17–18 mm. pressure, whereupon it practically all boiled from  $190^{\circ}$ – $193^{\circ}$ . This readily solidified and, on crystallizing from petroleum ether, it formed long, stout prisms,

melting at 49°–50°. It is extremely soluble in alcohol and benzene, and a nitrogen determination gave results agreeing with the calculated for *1-phenyl-5-methyl-3-ethoxytriazole*.

	Calculated for $C_{11}H_{13}N_3O$ .	Found.
N	20.7	20.9

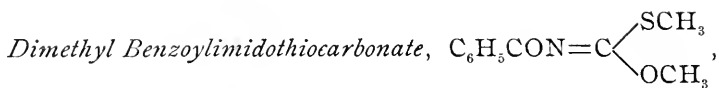
*On the Benzoylimidothiocarbonic Esters and Their Behavior with Hydrogen Chloride.*



We have prepared a series of these esters by treating the potassium salts of the benzoylthioncarbamic esters, in alcoholic solution, with alkyl iodides. Warming, during this process, must be avoided, since, otherwise, as found by Lössner in the case of the preparation of the diethyl ester,<sup>1</sup> mercaptan is evolved, and the oils suffer more or less decomposition with the formation of benzamide. The potassium salts of the benzoylthioncarbamic esters crystallize more readily than the sodium salts. In order to prepare them, alcoholic potash is added to a strong solution of the ester in alcohol when a crystalline mass separates at once. On treating the potassium salt of ethyl benzoylthioncarbamate suspended in alcohol with ethyl iodide, the mixture, after standing twelve hours, no longer had an alkaline reaction. Water was then added, and the precipitated oil was extracted with ether, washed, and then thoroughly dried over calcium chloride. On evaporating and distilling the oil at 19 mm. pressure, the material all boiled from 209°–212°, almost from the first to the last drop. There was no sign of decomposition and the yield is almost quantitative, a portion being lost in treating the alcohol solution with water. Thus obtained, ethyl benzoylimidothiocarbonate is a colorless oil of a faint odor, resembling the xanthic esters. Without further purification of the oil a nitrogen determination gave:

	Calculated for $C_{12}H_{15}NO_2S$ .	Found.
N	5.9	6.2

<sup>1</sup> *Loc. cit.*



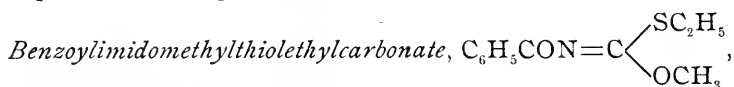
was obtained when 46 grams of methyl benzoylthioncarbamate, 9.5 grams of potassium hydrate, and 33.5 grams of methyl iodide were mixed in methyl alcohol. The mixture became warm, and the odor of mercaptan was noticed; this greatly increased on attempting to distil off the methyl alcohol after the action was complete. The heating was then stopped and cold water was added, and the oil was extracted with ether, whereupon, on evaporating, 22 grams of this ester were obtained, which, on standing, deposited plates of benzamide. These were filtered and the oil, without further purification, was used for the following experiments:

About 1 gram of the oil was dissolved in benzene and hydrogen chloride was passed in; warming and effervescence took place, and a mass of colorless needles separated, which melted from  $152^\circ$ – $153^\circ$  and were identical in every respect with *methyl benzoylthiolcarbamate*,  $\text{C}_6\text{H}_5\text{CO}-\text{NHCO}.\text{SCH}_3$ , described above.

Three grams of the oil were heated on the water-bath for about an hour and a half in a stream of hydrogen sulphide, mercaptan (?) and some methyl alcohol condensed in the delivery tube and, on cooling, dissolving in potassium hydrate and precipitating with hydrochloric acid, needles were obtained. When these were crystallized from dilute alcohol they were found to be *methyl benzoylthioncarbamate*,



described above. When this oil is allowed to stand in water it remains liquid for weeks. On exposure, the crude oil evaporated, leaving benzamide.



was prepared like the above diethyl ester. It was distilled at 20 mm. pressure when it boiled for the most part at about  $210^\circ$ . It then did not solidify in a freezing-mixture and in properties it resembled the diethyl compound. When this oil

was treated in dry benzene with hydrogen chloride it evolved methyl chloride and gave *ethyl benzoylthiolcarbamate*,



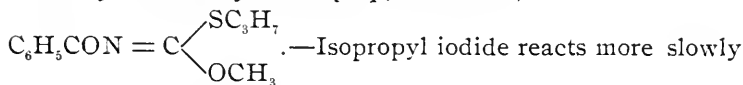
which, on evaporating the benzene and crystallizing from dilute alcohol, separated in long, slender prisms melting from  $105^\circ$ – $107^\circ$ . It is soluble in sodium hydrate, and a nitrogen determination gave :

	Calculated for $\text{C}_{10}\text{H}_{11}\text{NO}_2\text{S}$ .	Found.
N	7.0	6.7

An attempt to prepare this ester by warming ethyl thiolcarbamate,  $\text{H}_2\text{NCO}.\text{SC}_2\text{H}_5$ , with benzoic anhydride under conditions that were found to be favorable in the case of the corresponding acetyl compound, resulted in the formation of *cyanphenine* and a body which crystallized from alcohol in needles and melted finally from  $167^\circ$ – $168^\circ$ . This material contained sulphur, and a nitrogen determination gave results agreeing with the calculated for benzoyl rhodanide, the compound probably being the polymeric modification described by Miquel,<sup>1</sup> who states that it melts at  $160^\circ$ .

	Calculated for $(\text{C}_6\text{H}_5\text{CO}-\text{NCS})_3$ .	Found.
N	9.1	9.6

*Benzoylimidomethylthiolisopropylcarbonate*,



on the potassium salt of methyl benzoylthioncarbamate than the lower alkyl iodides. When 10 grams of the ester are used it is necessary to let the mixture stand for about three or four days. When the product was treated with hydrogen chloride it gave

*Isopropyl Benzoylthiolcarbamate*,  $\text{C}_6\text{H}_5\text{CONHCO}.\text{SC}_3\text{H}_7$ . — This crystallizes from alcohol in colorless prisms, which melt from  $136^\circ$ – $137^\circ$ . It is soluble in alkali, and a nitrogen determination gave :

	Calculated for $\text{C}_{11}\text{H}_{13}\text{NO}_2\text{S}$ .	Found.
N	6.2	6.2

<sup>1</sup> Ann. chim. phys. [5], 11, 269.

*Benzoylimidomethylthiolisobutylcarbonate,*

$\text{C}_6\text{H}_5\text{CON} = \text{C} \begin{cases} \text{SC}_4\text{H}_9 \\ \text{OCH}_3 \end{cases}$ , is an oil like the preceding. It required from two to three days for its preparation. When dry hydrogen chloride is led into its solution in benzene, it evolves methyl chloride and gives

*Isobutyl Benzoylthiolcarbamate*,  $\text{C}_6\text{H}_5\text{CONHCO}.\text{SC}_4\text{H}_9$ , which crystallizes from dilute alcohol in thin plates or scales and melts at  $115^\circ$ – $117^\circ$ . It is insoluble in water but readily soluble in benzene and sodium hydrate, and a nitrogen determination gave:

	Calculated for $\text{C}_{12}\text{H}_{15}\text{NO}_2\text{S}$ .	Found.
N	5.9	6.0

*Benzoylimidomethylthiolisoamylcarbonate,*

$\text{C}_6\text{H}_5\text{CON} = \text{C} \begin{cases} \text{SC}_5\text{H}_{11} \\ \text{OCH}_3 \end{cases}$ .—In this case the action was complete in two days, it being hastened finally by warming. The oil, without distilling, was dried in a vacuum at  $100^\circ$ , when a nitrogen determination indicated the presence of benzamide.

	Calculated for $\text{C}_{14}\text{H}_{19}\text{NO}_2\text{S}$ .	Found.
N	5.28	6.0

On standing, some benzamide separated. When this oil was treated with dry hydrogen chloride and the material purified by means of alkali and dilute alcohol, a compound crystallizing in needles was obtained, which melted at  $96^\circ$ . A nitrogen determination gave results which agreed with the calculated for *methyl benzoylthioncarbamate*, the calculated being 7.1 per cent, while 6.9 per cent was found. The calculated for the expected isoamyl benzoylthiolcarbamate is 5.5 per cent. The compound obtained had all the properties of the benzoylthionmethyl ester described above. This is the first exception to the rule that thiolcarbamic esters are formed by the action of hydrogen chloride on the imidothiolcarbonates.

*On the Behavior of Benzoylimidothiocarbonic Esters with Amines  
and on the Behavior of Benzoylpseudoureas with Hydrochloric Acid.*

As stated in the introduction, the behavior of the benzoyl-



imidothiocarbonic esters with bases has been investigated only in the case of ammonia.<sup>1</sup> We show below that the benzoylimidothiocarbonic esters readily react also with alkyl and aryl amines giving benzoylpseudourea ethers. Attempts to purify these compounds by distillation, in certain cases, were not crowned with success. Their behavior, however, with hydrochloric acid is described as the most characteristic reaction or simple test for their presence that we have observed, since by this treatment they evolve alkyl chloride and are, in most cases, quantitatively converted into the corresponding, easily crystallizable, benzoylureas.

*Benzoylpseudomethylurea*,  $\text{C}_6\text{H}_5\text{CO}-\text{N}=\text{C} \begin{matrix} \text{NH}_2 \\ \text{OCH}_3 \end{matrix}$ . — This

compound was prepared from benzoylimidomethylthiolisopropyl carbonate and alcoholic ammonia by allowing the mixture of these substances to stand for twelve hours, whereupon isopropyl mercaptan separated and the compound obtained by Dixon, in a similar manner, was obtained. It melted at  $77^\circ$  and agreed with his description. On treating this with 20 per cent hydrochloric acid, a reaction did not start immediately but, on gently warming, the material melted, then solidified, and, on crystallizing from alcohol, small lozenge-shaped plates separated, melting at  $214^\circ$  with effervescence. This material had all the properties of *benzoylurea*,



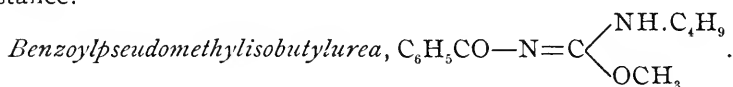
described above.

*Benzoylpseudomethylethylurea*,  $\text{C}_6\text{H}_5\text{CO}-\text{N}=\text{C} \begin{matrix} \text{NHC}_2\text{H}_5 \\ \text{OCH}_3 \end{matrix}$ .

—This was prepared from benzoylimidomethylthiolisopropyl carbonate by allowing a little less than 1 gram of the ester to stand for several days with a 33 per cent aqueous solution of ethylamine mixed with enough alcohol to form a solution. On then evaporating, an oil was obtained which was treated, without further handling, with 20 per cent hydrochloric acid, whereupon it was converted into

<sup>1</sup> Dixon : *Loc. cit.*

$\alpha, \beta$ -Benzoylethylurea,  $C_6H_5CONHCONHC_2H_5$ .—On standing, this separated from the hydrochloric acid solution in long needle-like prisms, some over 2 cm. in length. The preparation of this compound by a new method is of interest, because of the discrepancy between the melting-points recorded for this compound by Miquel,<sup>1</sup> Leuckart,<sup>2</sup> and Dixon.<sup>3</sup> These authors give  $192^\circ$ ,  $168^\circ$ , and  $114^\circ$ – $114.5^\circ$ . On crystallizing our material from petroleum ether it melted sharply at  $114^\circ$  and agreed in all respects with the compound prepared by Dixon from  $\alpha, \beta$ -benzoylethylthiocarbamide by desulphurization, so that evidently this is the correct melting-point for the substance.

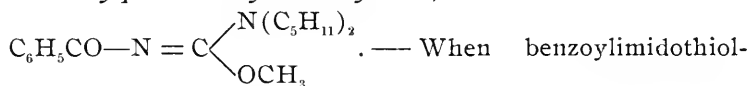


—When isobutylamine is mixed with benzoylimidomethyl thioethylcarbonate the mixture starts to boil immediately, giving off ethyl mercaptan, and cooling is necessary. The product is an oil which, when treated with hydrochloric acid, slowly gives off methyl chloride and solidifies, forming

*Benzoylisobutylurea*,  $C_6H_5.CONHCONHC_4H_9$ .—This was crystallized from alcohol when long, slender prisms were obtained, melting sharply at  $115^\circ$ . A nitrogen determination gave :

	Calculated for $C_{12}H_{16}N_2O_2$ .	Found.
N	12.7	12.9

*Benzoylpseudomethyl-diisoamylurea*,



methyl carbonate and diamylamine are mixed, reaction starts in the cold. The material was warmed to  $60^\circ$  until methyl mercaptan ceased being evolved, when hydrogen sulphide was passed in for several hours. On cooling, a mass of plates separated; these proved to be benzamide. On filtering and distilling at 13 mm. pressure, diisoamylamine, boiling at  $72^\circ$ , benzonitrile, and benzamide formed the chief products. An

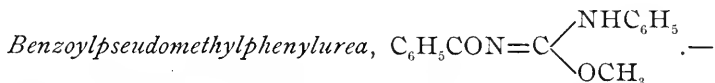
<sup>1</sup> Ann. chim. phys. [5], 11, 318.

<sup>2</sup> J. prakt. Chem. [2], 21, 33.

<sup>3</sup> J. Chem. Soc. (London), 1899, 383.

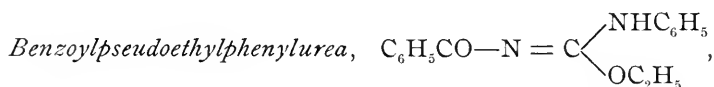
appreciable amount of diamylthionmethylcarbamate was not obtained.

This and the corresponding ethylbenzoylpseudourea ether differ from most of the other urea ethers that we have examined by the fact that, although they give off alkyl chloride with hydrochloric acid, nevertheless, a body corresponding to benzoyldiisoamylurea was not obtained. A number of experiments were tried with hydrochloric acid under different conditions, but in every case nothing but benzamide and diisoamyl hydrochloride could be isolated. This behavior is in accordance with the ease with which the addition-product in the case of ethyl benzoylthioncarbamate and diisoamylamine gives benzamide and free amine. When *pseudoethylbenzoyldiisoamylurea* was prepared from benzoylimidothioethylcarbonate and diamylamine, and the product treated with hydrochloric acid, ethyl chloride was evolved, and again nothing but benzamide and amine hydrochloride was found.



Benzoylimidomethylthioethyl carbonate and aniline readily react when mixed, and the action may be hastened by warming on the water-bath. After the evolution of ethyl mercaptan had ceased, in one experiment, we attempted to purify the product by distilling at 16 mm. pressure. Both the temperature and pressure rose steadily, the material beginning to boil at 70°. At this pressure, when the temperature rose to 200°, benzonitrile and other products distilled over, leaving a mass of tar in the distilling bulb.

When this crude pseudourea ether is treated with hydrochloric acid, it reacts at once, solidifying and giving off methyl chloride, and, on crystallizing the product from alcohol, benzoylphenylurea, melting at 202°–203°, is obtained. It is identical with the product obtained from ethylbenzoylthioncarbamate and aniline described above.

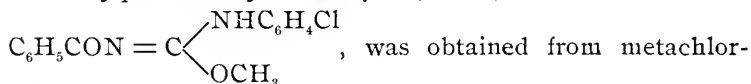


from 2 grams of aniline and 4.8 grams of benzoylimidothiol-

diethylcarbonate, formed a clear light-yellow oil, after heating for some time in a vacuum on the steam-bath. A preparation made in this manner was analyzed with the following result :

	Calculated for $C_{16}H_{16}N_2O_2$ .	Found.
N	10.4	10.8

*Benzoylpseudomethyl-m-chlorphenylurea*,



aniline and benzoylimidomethylthioethyl carbonate after eight hours' heating on the water-bath. It was converted directly by hydrochloric acid into *benzoylmetachlorphenylurea*,



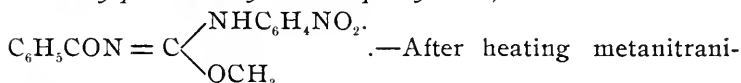
which crystallizes in needles from alcohol, melting at about  $200^\circ$ . We were unable to obtain all the nitrogen from this compound on burning with copper oxide in the usual manner. Two determinations gave 8.60 and 8.64 per cent of nitrogen, while the calculated is 10.2 per cent. In order to determine whether this peculiarity is the fault of the analytical method and whether the above compound is the benzoylurea in question, we prepared this benzoylmetachlorphenylurea by desulphurizing *benzoylmetachlorphenylthiourea*,



in regard to the structure of which there can be no question, since it was prepared from pure benzoyl rhodanide and colorless metachloraniline, the latter boiling from  $229^\circ$  to  $231^\circ$ . Here, again, we had the same difficulty on analysis; a determination gave 8.4 per cent instead of 9.6 per cent nitrogen. This material crystallizes from alcohol in colorless needles melting at  $125^\circ$ . On boiling the alcoholic solution of this compound with silver nitrate and a little water, a compound was obtained which crystallized in needles and melted at  $200^\circ$ . It was identical in every respect with the above compound obtained from the pseudourea ether. And when portions of the two samples were mixed the melting-point was not altered. It follows, therefore, that the material is the urea in question

and that this urea and thiourea do not give up all their nitrogen under the usual conditions of a nitrogen determination.

*Benzoylpseudomethyl-m-nitrophenylurea*,

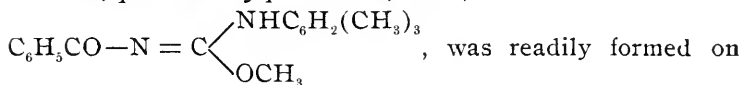


with benzoylimidomethylthioethyl carbonate for four or five hours on the water-bath the evolution of ethyl mercaptan ceased. The oil thus obtained was treated with hydrochloric acid, whereupon it changed to a crystalline mass. This was washed with water and crystallized from alcohol, whereupon it gave

*Benzoylmetanitrophenylurea*,  $\text{C}_6\text{H}_5\text{CONHCONHC}_6\text{H}_4\text{NO}_2$ .—This is insoluble in water and chloroform and difficultly soluble in benzene and alcohol. From the latter solution it separates in the form of fine, short needles, which melt from  $231^\circ$ – $232^\circ$ . A nitrogen determination gave:

	Calculated for $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_4$	Found.
N	14.7	14.4

*Benzoylpseudomethylpseudocumylurea*,



warming benzoylimidomethylthiolmethyl carbonate and pseudocumidine. On cooling, the mass was treated with hydrochloric acid, whereupon methyl chloride escaped and, on washing with water and alcohol and crystallizing from chloroform, a woolly mass of very bulky, long needles was obtained. This substance melted at  $207^\circ$  and on analysis proved to be

*Benzoylpseudocumylurea*,  $\text{C}_6\text{H}_5\text{CONHCONHC}_6\text{H}_2(\text{CH}_3)_3$ .

	Calculated for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_2$	Found.
N	9.92	9.78

*Benzoylimidomethylthiolisobutyl carbonate and methylaniline* reacted very slowly, giving off mercaptan. After warming on the water-bath for three days, an oil was obtained that had a beautiful purple color. It did not readily solidify with hydrochloric acid and, therefore, it was not further examined.

Contributions from the Chemical Laboratory of Bryn Mawr College.

## ON SOME ISOMERIC HALOGEN COMPOUNDS OF THALLIUM, AND THE CONSTITUTION OF DOUBLE SALTS.

[FIRST PAPER.]

BY ALLERTON S. CUSHMAN.

### *Introduction.*

Thallium forms simple salts with the halogens<sup>1</sup> of the general types  $TlX$  and  $TlX_3$ . The compounds of the type  $TlX$  resemble in color and general appearance the corresponding silver salts, and like the latter are precipitated by the halogen acids. The thalious halides are, however, appreciably soluble in water, in which respect they resemble the corresponding compounds of lead. The thallic salts of the type  $TlX_3$  are very soluble in water, in which solvent they are more or less hydrolyzed, the solution becoming acid while the insoluble oxide,  $Tl_2O_3$ , is formed. The instability of these compounds makes it extremely difficult, if not impossible, to isolate them in pure condition. The assignment to them of the formula  $TlX_3$  rather than the double formula  $Tl_2X_6$  is a purely arbitrary matter resting on no experimental evidence whatever.

Thallium, in its higher state of valence, forms well-defined double salts with many other metals of the general types  $TlX_3.RX$  and  $TlX_3.3RX$ .

In 1863 Crookes and Church<sup>2</sup> discovered a sesquichloride of thallium which has a formula corresponding to  $Tl_2Cl_3$ . In 1865 an extended study of the compounds of the then newly discovered element was carried on by Willne.<sup>3</sup> In his paper Willne sums up the reasons for believing that the compounds of the types  $TlX_2$  and  $Tl_2X_3$ , respectively known as the tetra-

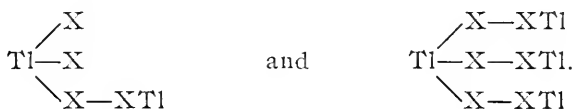
<sup>1</sup> As only the chlorides and bromides are considered in this paper the word halogen is used throughout as referring to chlorine and bromine only.

<sup>2</sup> Chem. News, 8, 1.

<sup>3</sup> Ann. chim. phys., 5, 4 (1865).

and sesqui-salts should be considered as true double salts, and be written  $TlX_3.TlX$  and  $TlX_3.3TlX$ . In a few words the reasons may be given as follows: (1) These intermediate halogen compounds of thallium resemble in their behavior certain well-known double salts, such as  $TlCl_3.CuCl$ ,  $TlCl_3.3KCl$ ,  $TlCl_3.3NH_4Cl$ , etc. (2) When a mixture of solutions of thallos and thallic halides in the proper proportions is made the intermediate thallium compounds are obtained. (3) There are no oxides known corresponding to these intermediate salts, and, if the latter are treated with an alkali, they decompose, forming the alkaline halide, and, on the one hand, the insoluble thallic oxide, and, on the other, the thallos halide. Subsequent work has confirmed the view that these compounds are to be considered as true double salts.<sup>1</sup> Thallium sesquichloride has been made heretofore.<sup>2</sup> By heating the dry chloride,  $TlCl_3$ , somewhat above  $100^\circ$  as long as chlorine is given off, the brown liquid cools to a clear lemon-yellow mass (Lamy); also by precipitating a solution containing a mixture of thallos and thallic salts with hydrochloric acid (Willne); also by dissolving thallium or thallos chloride in aqua regia and evaporating (Crookes and Church).

It seemed that these peculiar double salts which thallium has the power of forming with itself might throw some light on the ingenious and alluring theory of Werner<sup>3</sup> on the constitution of double salts. Adopting the older theory of Blomstrand-Jørgensen as developed by Remsen<sup>4</sup>, we should write the tetra- and sesqui-salts, respectively:



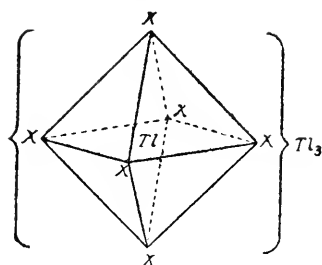
According to Werner, on the other hand, we have in the case of the sesqui-salt a dominant thallium atom at the center of an octahedron, thus:

<sup>1</sup> Neumann: *Ann. Chem. (Liebig)*, **244**, 329.

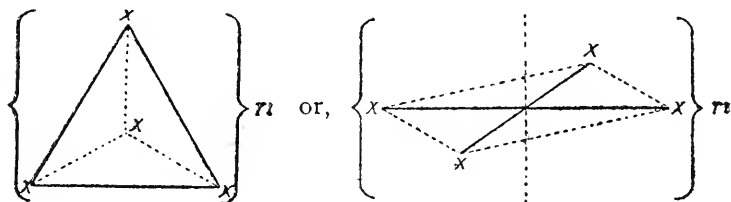
<sup>2</sup> Watts' Dictionary (Muir and Morley), 1894.

<sup>3</sup> *Ztschr. anorg. Chem.*, **3**, 267, et seq.

<sup>4</sup> This JOURNAL, **11**, 291.



In the case of the tetra salt we can suppose the dominant thallium atom to be at the center of a tetrahedron or we can assume a configuration of the molecule in a plane where one axis from the above type is unsaturated. Thus :



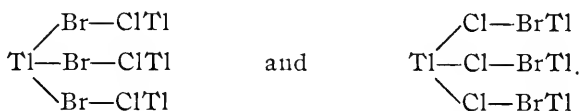
On this hypothesis we should write these compounds ordinarily  $(Tl'''X_6)_3Tl'$  and  $(Tl'''X_4)Tl'$ . Following the assumption to its logical conclusion, we should write thallic chloride not  $TlCl_3$  but  $(Tl'''Cl_6)Tl'''$ .

The fact that no penta halogen compounds of thallium are known to exist would seem on first thought to favor the hypothesis of Werner. According to the older theory,  $TlCl_3 \cdot 2TlCl$  should be quite as capable of existence as  $TlCl_3 \cdot TlCl$ . We must consider, however, that the tetrahedral and octahedral spatial symmetries were selected to fit the greatest number of known salts. The selection of these two types by no means exhausts the possibilities, and if compounds corresponding to a five symmetry should be obtained, they could be accounted for as well by one theory as by the other.

It seemed likely that under either of these theories it might be possible to form mixed double salts of thallium in which bromine atoms should be substituted for chlorine atoms, and *vice*



*versa*. Thus, for instance, we could expect isomeric forms, such as<sup>1</sup>



Under the older theory if these compounds were capable of existing, the isomerism would be simply a case of linkage, whereas, under Werner's theory, we should have true spatial isomerism. It was realized that a study of such isomerism and the collection of all possible evidence as to the way these compounds dissociate in solution would be of the greatest interest. Although the work is as yet uncompleted, enough has been done to justify this preliminary paper.

#### *Preliminary Work.*

At the beginning of the investigation it was noted that when chlorine is passed through water in which an excess of thallous chloride is suspended, the white color of the chloride changes gradually to lemon-yellow. If the chlorine is allowed to pass to complete saturation, the yellow compound finally disappears, owing to the formation of the exceedingly soluble thallic chloride. As the sesquichloride is to a high degree insoluble in the cold,<sup>2</sup> it was to be expected that the definite sesquichloride stage would be reached by this reaction before a notable quantity of the thallic salt formed and went into solution. It, therefore, seemed probable that this method would furnish a convenient way of making these double salts. A doubt remained whether the sesquichloride stage may be considered as of definite composition, or whether in passing from the thallous to the thallic state we may not obtain mixtures of variable composition.<sup>3</sup> The fact that the yellow compound is soluble in hot water, from which it crystallizes, on cooling, in brilliant hexagonal leaflets,

<sup>1</sup> The failure of R. W. Atkinson to obtain isomeric forms of  $\text{SbCl}_{3.3}\text{KBr}$  was not known to the author until after the work here described was completed. Compare *J. Chem. Soc.*, **43**, 289 (1883).

<sup>2</sup> One part in 380.1 parts water at 15°; 52.9 at 100°. Crookes, Hebbeling: *Ann. Chem. (Liebig)*, **134**, 21.

<sup>3</sup> Doubts on this head have been hitherto expressed. Compare Werther: *J. prakt. Chem.*, **91**, 390.

which under a high-power microscope present every evidence of individuality, seemed to support the first assumption. Manifestly, however, complete quantitative evidence was needed of a more careful nature than any that was available in the literature. Neumann has claimed that the addition of chlorine to thallous chloride leads to the formation of the tetrachloride as well as of the sesqui-salt. As the point is important the paragraph is quoted in full :<sup>1</sup> "Als Ausgangsmaterial für diese Präparate diente mir anfangs Thallchlorid. Diese Verbindung ist frei von Oxydul-salze ziemlich schwer herzustellen, denn das Chlorid hat grosse Neigung in das Chlorür überzugehen was schon daraus erhellt, dass beim Lösen von Thalli-oxyd in Salzsäure immer Chlorür in nicht unbeträchtlicher Menge über dem Chlorid entsteht. Beide Salze vereinigen sich hierbei theilweise zu Doppelverbindungen von den Formeln  $2\text{TlCl} \cdot \text{Tl}_2\text{Cl}_6$  und  $6\text{TlCl} \cdot \text{Tl}_2\text{Cl}_6$ . Salze in denen  $\text{Tl}_2\text{Cl}_6$  und  $\text{TlCl}$  in Verhältniss 3 : 4 und 15 : 1 stehen, habe ich nicht erhalten, wohl aber Gemische von  $2\text{TlCl} \cdot \text{Tl}_2\text{Cl}_6$  und  $6\text{TlCl} \cdot \text{Tl}_2\text{Cl}_6$  auch mit  $\text{Tl}_2\text{Cl}_6$ . Aus solchen Gemischen, ferner aus Thallochlorid wie auch aus metallischem Thallium, erhält man die Lösung des reinen Chlorids, wenn man die genannten Stoffe in Wasser suspendirt mit Chlor behandelt."

Neumann was unable to determine the chlorine in his salts and depended on estimations of thallium alone. An electrolytic method was used and only one determination of thallium for each salt is published. Particulars beyond those quoted above are not given, and it is not apparent how the tetrachloride was made and separated from the sesqui salt. Lamy obtained the tetrachloride in the dry way by passing chlorine over fused thallous chloride, the heat being very carefully controlled. The compound was found to pass readily into the sesqui-salt. Willne<sup>2</sup> was never able to obtain it by any other method than that followed by Lamy, and every effort to obtain it in the wet way in this investigation has resulted in failure. The large preponderance of evidence seems to point to the conclu-

<sup>1</sup> Neumann: Ueber Doppelsalze von Sesquichloriden. Ann. Chem. (Liebig), **244**, 344.

<sup>2</sup> Willne: Loc. cit.

sion that the tetrachloride cannot exist in solution, the sesquichloride alone being formed.

*Preparation of Pure Material.*

The material which formed the basis of this investigation consisted of a mass of metallic thallium which contained as impurities a considerable quantity of lead and traces of copper and silver. In order to purify the material it was dissolved in sulphuric acid and the clear solution, after dilution, decanted from the insoluble lead sulphate. Hydrogen sulphide was then passed in and the copper and silver sulphides, together with some reddish sulpho-compound of thallium that formed, filtered out. After boiling off the excess of hydrogen sulphide this strong solution of thallous sulphate which gave no precipitate with sodic carbonate and showed with the spectroscope no alkaline impurities beyond traces of sodium, was used as the starting-point in the preparation of all the compounds hereafter described. The thallous halides, after precipitation with the pure halogen acids, were washed with cold water until quite free from sulphuric acid.

*Methods of Analysis.*

The quantitative determination of thallium in its compounds has presented difficulties to many experimenters, owing to the solubility of nearly all the compounds of this peculiar metal. Evidently the thallium chloroplatinate is the ideal salt through which most accurately to determine thallium, as it has been shown by Crookes to be insoluble in 15,580 parts of water at 15°. This is clearly admitted by Willne<sup>1</sup> as well as by Neumann,<sup>2</sup> but the method was discarded by both these experimenters on account of the tendency of the precipitate to pass through the filter. As carried out in this laboratory, the method presents no difficulties, and may be classed among the easiest and most rapid of accurate gravimetric operations. The hot thallium solution which, if not already in the lower state of oxidation, must be reduced by addition of sulphurous acid until the smell of sulphur di-

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Ueber die quantitative Bestimmung des Thalliums. *Ann. Chem. (Liebig)*, 244, 349.

oxide in excess is apparent. The liquid is then carefully brought to boiling and an excess of platinic chloride added. The flask is then closed tightly with a smooth rubber stopper and the contents vigorously shaken for five minutes. After cooling, the precipitate will be found an ideal one to work with. It neither "creeps" nor clings to the glass; it is easily filtered and washed on a Gooch crucible, dries quickly, and is not hygroscopic. In drying, the precaution was taken not to allow the temperature of the oven to rise above  $100^{\circ}$ , as it has been found that the precipitate begins to decompose at a little above  $100^{\circ}$ , whereas it seems to have no tendency to retain water below  $100^{\circ}$ , and can even be brought to constant weight in a desiccator over caustic soda. This method has been used throughout this investigation, and has been found most satisfactory.

The estimation of the halogen in these compounds was complicated with difficulties. According to Neumann:<sup>1</sup> "Thallium hat die unangenehme Eigenschaft, bei der Bestimmung des Chlors in seinen salzsauren Salzen mit dem Silberchlorid theilweise auszufallen."<sup>2</sup> Da also nur mangelhafte Resultate erhalten werden konnten verzichtete ich auf die Chlorbestimmungen."

In this laboratory it was found that from a solution of a thalious halide the silver halide is as accurately precipitated as is the case with other soluble halides of monovalent metals. In the case of the thallic, as well as the intermediate double salts, we meet with an entirely different state of affairs. When silver nitrate is added to a neutral solution of one of these salts, a chocolate-brown precipitate is invariably obtained. It was found, however, that, in the presence of a sufficient quantity of nitric acid, the silver halide came down without occluding thallium. This was proved by careful spectroscopic examination of the washed precipitates as well as by abundant quantitative evidence. In analyzing these salts the following method has been found quite satisfactory: The salts are dissolved by boiling in 10 per cent nitric acid, an excess of silver nitrate is added, and the carefully stoppered flask vigor-

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Compare Werther: *Ztschr. anal. Chem.*, 3, 1.

ously shaken. The silver halide is filtered on a Gooch crucible, washed, and weighed with the usual precautions. The composition of the dark-colored precipitate which comes down from neutral solutions will be shown later in this paper.

### *Preparation of Compounds.*

In order to see if the sesquichloride of thallium could be obtained in a perfectly definite state, chlorine was passed through water, in which pure thallos chloride was suspended, until the white color of the chloride had completely turned to yellow. Some of this yellow compound was now removed and called Sample I(a). Chlorine was then passed into the residue until the yellow substance had nearly, but not quite, gone into solution. This last yellow residue was washed by decantation and called Sample I(b). Both samples were now twice recrystallized from water barely acidified with nitric acid. The sesqui as well as the thallic, thallium compounds are slightly hydrolyzed in water solution with separation of insoluble thallic hydroxide. The presence of nitric acid prevents this separation. The two samples prepared in this way presented precisely the same appearance, both to the eye and under a powerful microscope. When magnified 84 diameters they appeared as shining hexagonal plates of a delicate, lemon-yellow color. The analyses of these compounds are given below :

- I(a). 1.4585 grams compound yielded 1.2132 grams AgCl.  
 1.2752 grams compound yielded 2.0150 grams  $\text{PtCl}_4 \cdot 2\text{TlCl}$ .
- I(b). 1.4720 grams compound yielded 1.2303 grams AgCl.  
 1.2579 grams compound yielded 1.9901 grams  $\text{PtCl}_4 \cdot 2\text{TlCl}$ .

	Calculated for $\text{TlCl}_{3.3}\text{TlCl}$ .	I(a).	Found. II(b).
Tl	79.33	79.08	79.23
Cl	20.67	20.56	20.67
	<hr/> 100.00	<hr/> 99.64	<hr/> 99.90

These analyses show that these samples are essentially the same.

In order to study the reaction which takes place when sil-

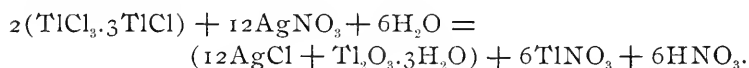
ver nitrate is added to a neutral solution of the sesquichloride, weighed quantities of the latter were dissolved in as little water as possible to avoid hydrolysis, and an excess of a solution of silver nitrate added; the analysis was then carried out in the usual way.

1.4426 grams compound yielded 1.5230 grams dark precipitate.

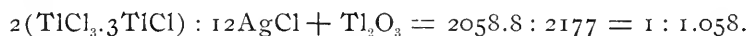
1.2192 grams compound yielded 1.2910 grams dark precipitate.

Calculated for 1 gram of the substance we obtain the ratios 1 : 1.054 and 1 : 1.059.

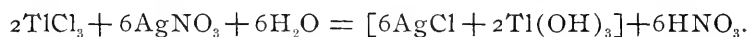
These are satisfied by the following equation :



The dark precipitate is represented by the part of the equation in parenthesis. After drying and weighing we have the ratio :



For thallic chloride the reaction may be written as follows :

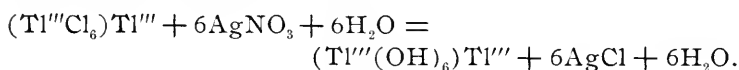


We have in these reactions an interesting case of reversible equilibrium, depending upon the mass of the nitric acid, thus :

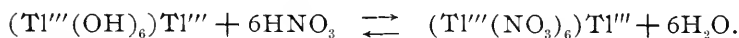


Considered in the light of Werner's hypothesis these reactions are of interest. If we are to write the sesqui and thallic compounds, respectively, as  $(\text{Tl}^{\text{III}}\text{Cl}_6)_3\text{Tl}^{\text{I}}$  and  $(\text{Tl}^{\text{III}}\text{Cl}_6)\text{Tl}^{\text{III}}$ , we should not expect chlorine ions to be present in solution, and the fact that both salts give instantaneous precipitates with silver nitrate would seem to be opposed to Werner's theory. On the other hand, it is probable that there would be a continual tendency for the halogen atoms in the complex nucleus, to be substituted by hydroxyls as is shown by the readiness with which these substances hydrolyze in solution. In view of the delicate equilibrium which determines this secondary dissociation, it does not seem improba-

ble that the addition of silver nitrate solution with its strongly positive silver ions would disturb the equilibrium and start the reaction which then proceeds rapidly to completion. On this assumption we should write the reaction as follows :



Similarly, the reversible reaction becomes :

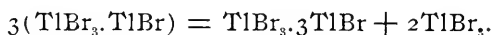


We have here a case of the octahedral spatial symmetry, and the direction of the reaction is conditioned under the Mass Law by the power of the hydroxyl and nitroxyl groups, respectively, to occupy the points of symmetry. Although what is here given extends the theory of Werner to include simple as well as so-called double salts, it is not advanced as a speculation, but as a logical result of the application of Werner's hypothesis to these reactions.

#### *Preparation of the Tetra- and Sesquibromides.*

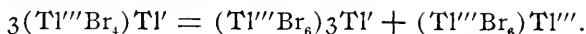
These compounds were first prepared by Willne.<sup>1</sup> When thallous bromide suspended in very little water is treated with bromine, a yellow compound is formed, which dissolves on heating, and crystallizes on cooling in beautiful, minute, yellow needles which, under the microscope, appear as elongated quadratic prisms. On dampening the yellow crystals with water, they immediately assume a brilliant, scarlet hue. On dissolving in water and recrystallizing, dark-red crystals appear in the form of small, hexagonal plates. According to Willne's analyses, confirmed in this laboratory, the yellow needles are the tetrabromide, and the red, hexagonal crystals the sesquibromide. Throughout the study of these compounds it has been noticed that the tetra-salts crystallize in square prisms, whereas the sesqui-salts invariably appear in hexagonal forms.

The reaction that takes place in the presence of water can be written :



<sup>1</sup> *Loc. cit.*

According to Werner we may write :



It is only necessary to assume that in the presence of water the tendency of these thallium compounds is to assume the octahedral symmetry rather than the unsaturated configuration with the four bromine atoms in a plane, and the above reaction represents the only possible rearrangement. This would also account for the fact that in the case of the chlorine compound, the more active chlorine atoms do not permit the formation of a tetra salt in the wet way.

#### *Isomeric Double Salts.*

Since the treatment of thallous chloride with thallic chloride leads to the formation of a double salt,  $\text{TlCl}_3 \cdot 3\text{TlCl}$ , it seemed possible that the treatment of thallous bromide with thallic chloride would lead to  $\text{TlCl}_3 \cdot 3\text{TlBr}$ , while on the other hand the treatment of thallous chloride with thallic bromide would lead to the isomeric compound  $\text{TlBr}_3 \cdot 3\text{TlCl}$ . In the first place, however, it seemed desirable to study the reaction of bromine on moist thallous chloride. Pure bromine was shaken up with thallous chloride in the presence of water until the white color of the thallous salt had changed to orange-yellow. The orange-colored substance was washed by decantation with cold water, and finally dissolved in boiling water barely acidified with nitric acid. On cooling, dark, orange-colored, hexagonal plates separated. These crystals were similar in form, but coarser and of a much darker color than the sesquichloride compound already described. After two recrystallizations, the compound was washed, dried, and prepared for analysis.

It is apparent that we have here an analytical problem of some difficulty. Theoretically, we should expect the formation of the compound,  $\text{TlClBr}_2 \cdot 3\text{TlCl}$ . If the silver halides are precipitated together and the thallium separately determined, data are obtained from which, by indirect methods, the full percentage composition of the compound can be calculated. Only sufficient data will be inserted here to show that the compound really corresponded to the formula given above.



I. 1.1466 grams compound yielded 0.9703 gram silver halide.

II. 1.2203 grams compound yielded 1.0270 grams silver halide.

I. 1.0290 grams compound yielded 1.4998 grams  $\text{PtCl}_4 \cdot 2\text{TlCl}$ .

II. 1.3545 grams compound yielded 1.9745 grams  $\text{PtCl}_4 \cdot 2\text{TlCl}$ .

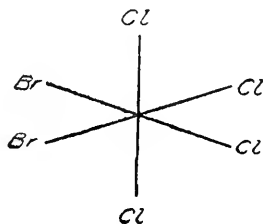
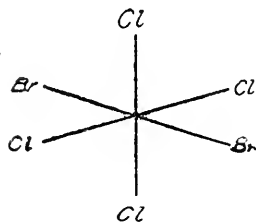
	Calculated for $\text{TlClBr}_2 \cdot 3\text{TlCl}$ .	I.	Found.
Halogen	26.99	26.90	26.76
Th	73.01	72.91	72.96
	<hr/>	<hr/>	<hr/>
	100.00	99.81	99.72

Calculating by the method of "indirect analysis" we have from I.

	Calculated.	Found.
Cl	12.67	12.50
Br	14.32	14.40
Tl	73.01	72.91
	<hr/>	<hr/>
	100.00	99.81

The theoretical composition of this double salt is thus shown to be the true one. Working by analogous methods, it should be possible to form  $\text{TlCl}_2\text{Br} \cdot 3\text{TlBr}$  as well as  $\text{TlCl}_2\text{Br} \cdot 3\text{TlCl}$  and  $\text{TlBr}_2\text{Cl} \cdot 3\text{TlBr}$ . None of these compounds has as yet been made. As they would not be isomeric with each other, their study has been reserved for a future occasion.

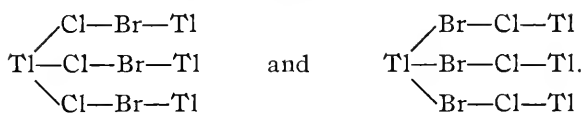
Writing the compound  $\text{TlClBr}_2 \cdot 3\text{TlCl}$  according to Werner's hypothesis, we have  $(\text{Tl}''' \begin{smallmatrix} \text{Cl}_4 \\ \text{Br}_2 \end{smallmatrix})_3\text{Tl}'$ . It is at once apparent that too spatial isomers are theoretically possible, as represented in the following diagrams:



Compound No. I, of the two whose analyses are given above was made as described, by treating thallous chloride with bromine. Compound No. II was made by treating more thallous chloride suspended in water with the decanted mother-liquor from I. The reaction in the latter case went on in more dilute solution and away from the influence of free bromine. Compound No. I had an orange-yellow color. Compound No. II had a lemon-yellow color, and these separate colors were held through two recrystallizations from dilute nitric acid. The exciting question arose as to the possible isomerism of these two preparations. Every effort was made to get light on the subject, but without success. Mixtures of the two samples were made and subjected to fractional crystallization, but medium-colored crystals were obtained at each end of the fractionation. The melting-points seemed to be the same. Under the microscope the crystal forms were identical, only the shade of color being different. If these compounds are indeed isomeric, they resemble each other so closely in physical characteristics that it is impossible to distinguish them from each other. On the other hand, it is possible that the different shades of color have nothing to do with isomerism, but are due to crystal aggregation or minute traces of impurity in one case or the other. Further work is needed to decide this question.

*Trichlorbromides and Tribromchlorides.*

When thallous bromide, suspended in hot water, is treated with a dilute solution of thallic chloride, an orange-colored compound is formed which can be dissolved by boiling. On cooling, orange-colored, hexagonal plates are deposited which resemble in general appearance Compound No. I, described above. On the other hand, when thallous chloride is suspended in a considerable quantity of hot water and treated with a hot solution of thallic bromide, a dark, blood-red compound is formed which dissolves on boiling, and, on rapid cooling, crystallizes out in beautiful, blood-red, hexagonal crystals. Written according to the older theory, these compounds should be respectively :



In these compounds we have a case of true isomerism which can be accounted for by either of the theories for the constitution of double salts under discussion. The orange isomer is very stable and can be crystallized out of water unchanged; the red isomer, on the other hand, is very unstable and is easily decomposed by water, and even by alcohol and ether. It can, however, be recrystallized unchanged out of its own mother-liquor, even after the mother-liquor has been considerably diluted. In working with this compound, a very curious example of equilibrium was noticed. As the mother-liquor is gradually diluted, a point is reached where the clear, boiling liquid, on being allowed to cool, slowly deposits a buff-colored precipitate which has the appearance of a thallos compound whose color is modified by occlusion of some sesqui salt. If, however, the boiling liquid is cooled suddenly by plunging the flask into cold water, the blood-red crystals are deposited without a sign of decomposition.

From these facts it appears that, on solution, the salt  $\text{TlBr}_3 \cdot 3\text{TlCl}$  dissociates into  $\text{TlBr}_3$  and  $3\text{TlCl}$ , and that the compound that will appear on cooling is conditioned by an equilibrium depending on the temperature and the solubility of the products of the thallos salt and the double salt, respectively. On the other hand, if  $\text{TlBr}_3$  and  $\text{TlCl}$  exist in solution, and these compounds are in turn dissociated so that halogen ions exist, it is difficult to see why both isomers, on recrystallization, retain their characteristic individuality instead of, at least in part, passing into each other. Undoubtedly we have here a problem of great theoretical interest, though one which presents great difficulties. On first thought, the facts as stated do not seem to find any explanation under the theory of Werner, but it is possible that a condition of affairs which exists at a certain temperature and state of equilibrium is quite different at higher temperatures. In this connection it can be said that ammonium chloride can

be written on the tetrahedral type as  $\left( \begin{array}{c} \text{H} \\ | \\ \text{H}-\text{N}-\text{H} \\ | \\ \text{H} \end{array} \right) \text{Cl}$  only

at a certain equilibrium, conditioned by the temperature. The fact that above a certain temperature we have  $(\text{NH}_3)$   $(\text{HCl})$  does not effect our belief in  $\text{NH}_4\text{Cl}$ . All the phenomena observed in this investigation point to the conclusion that the double salts do not exist in solution above certain definite temperatures. This point will be taken up again later on. Before proceeding it will be necessary to insert a sufficient amount of the analytical data obtained, to prove the composition and isomerism of these salts. There was no difficulty in preparing the orange compound for analysis, the red compound could only be washed with carbon disulphide, and it was impossible to free it entirely from its own mother-liquor.

#### *Analysis of Orange Compound.*

1.1812 grams compound yielded 1.0108 grams silver halide.  
0.8969 gram compound yielded 1.2570 grams  $\text{PtCl}_{4.2}\text{TlCl}$ .

#### *Analysis of Red Compound.*

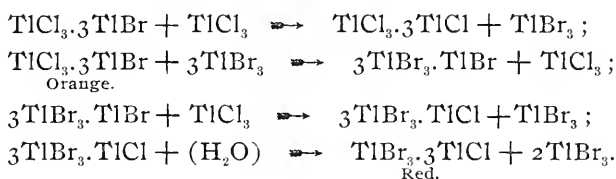
0.9515 gram compound yielded 0.8210 gram silver halide.  
1.0098 grams compound yielded 1.4139 grams  $\text{PtCl}_{4.2}\text{TlCl}$ .

	Orange compound.		Red compound.	
	Calculated.	Found.	Calculated.	Found.
Cl	9.15	9.19	9.15	9.50
Br	20.63	20.59	20.63	20.24
Tl	70.22	70.14	70.22	70.07
	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	99.92	100.00	99.81

Since these compounds appear to be isomeric, it seemed likely that, by varying the equilibrium, some means might be found to pass directly from one to the other. If the orange compound,  $\text{TlCl}_{3.3}\text{TlBr}$ , is treated with an excess of thallic chloride,  $\text{TlCl}_3$ , the orange color gradually turns to a lemon-yellow and, on recrystallization, the sesquichloride,  $\text{TlCl}_{3.3}\text{TlCl}$ , is obtained. This was proved by several concordant

analyses of the lemon-yellow compound. On the other hand, if the orange compound is treated with a strong solution of thallic bromide,  $\text{TlBr}_3$ , long, yellow needles are obtained which, when treated with water and recrystallized, yield dark-red crystals of a sesqui-compound.

On analysis, as given below, the long, yellow needles correspond to the formula  $\text{TlBr}_3 \cdot \text{TlCl}$ . The change which takes place in passing from the orange to the red compound is indicated by the following reactions:



In the process of making the red compound by treating thallic chloride with thallic bromide, it was found possible by varying the dilution to obtain directly either yellow needles, the orange compound, or the red compound. At a certain definite point in the equilibrium, the hot solution, on cooling, may begin to deposit the orange compound. As this salt continues to settle out of the solution, the relative amount of thallic bromide present is constantly increasing, until at a certain point in the equilibrium, suddenly the long, yellow needles are seen to be forming on top of the orange, hexagonal plates, and the reaction then continues until not a vestige of the orange compound remains. This curious and interesting phenomenon has been observed over and over again in this laboratory, and it has even been found possible to adjust the equilibrium so delicately that, if the solution is suddenly cooled, the orange compound will be deposited, whereas, if gradually cooled, only the yellow needles of the tetra compound are obtained.

A question that naturally arises and one that every effort has been made to answer, is whether indeed the yellow needles correspond to the formula  $\text{TlBr}_3 \cdot \text{TlCl}$  and are not in part or entirely  $\text{TlBr}_3 \cdot \text{TlBr}$ . In the latter case it might be doubted whether the red compound was in truth isomeric with the orange compound, but was not rather the sesquibromide.

a mixture of the latter with the orange compound. The final appeal must be to as careful quantitative analysis as is possible under the circumstances, but, first of all, qualitative evidence was sought. Some of the yellow needles were powdered together with potassium bichromate and the mixture heated with strong sulphuric acid. The vapor from this reaction, when passed through dilute ammonia, invariably gave a slight amount of yellow ammonium chromate. Samples of the true tetrabromide gave no ammonium chromate when treated in exactly the same way.

The foregoing considerations will make it apparent that the preparation and analysis of the tetrahalogen compound in question presents many difficulties. The crystals cannot be washed except with carbon disulphide, and it is therefore difficult to obtain them free from the mother-liquor. Determination of the halogen content does not aid in distinguishing between  $\text{TlBr}_3 \cdot \text{TlBr}$  and  $\text{TlBr}_3 \cdot \text{TlCl}$  as the analytical data fit either salt equally well. The only recourse was to the determination of the thallium, but, even in this case, it must be remembered that, as the two compounds are isomorphous, the preparation of  $\text{TlBr}_3 \cdot \text{TlCl}$  quite free from  $\text{TlBr}_3 \cdot \text{TlBr}$  must be a matter of difficulty, if it is not quite impossible. A large number of analyses of the yellow needles were made. Four of these, including the two worst and the two best, are tabulated below:

No. of analysis.	Weight substance taken.	Weight $\text{PtCl}_{4,2\text{TlCl}}$ found.	Thallium. Per cent.
6	1.0006	1.1812	59.07
4	1.0016	1.1880	59.36
3	1.0234	1.2199	59.67
2	0.7658	0.9140	59.71

Average, 59.45

The theoretical percentage composition of the two salts is as follows:

	$\text{TlBr}_3 \cdot \text{TlCl}$ .	$\text{TlBr}_3 \cdot \text{TlBr}$ .
Tl	59.70	56.06
Halogen	40.30	43.94
	<hr/> 100.00	<hr/> 100.00

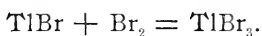
From the foregoing considerations it seemed that the isomerism of the orange and red compounds might be safely assumed, but it remained to be seen if any further light could be thrown on the question of their constitution. In order to get an idea of the way these compounds primarily dissociate, crystals of the orange and of the red substances were sealed up separately in stout glass tubes under their own mother-liquors, and then gradually heated in a sulphuric-acid bath. At about  $100^{\circ}$  a change in color was noticed, and, gradually, as the temperature rose, white precipitates resembling the thalious halides alone remained in the tubes. On cooling again, the double salts re-formed in well-defined crystals until finally no sign of the white thalious salt was left. It was apparent that above a certain temperature the double salts did not exist.

*Physical Measurements.*

It was hoped that a study of the electrical conductivity of the thallium halides in solution might shed some light on the constitution of the double salts. Unfortunately, both the thallic and the sesquithallium compounds are hydrolyzed to a certain extent in solution. While this fact prevents any accurate measurements of the conductivity due purely to the ionization of the salts, nevertheless, results can be obtained which are of value. The measurements were made by the usual Kohlrausch method in a cell of the Arrhenius type. The thermostat was kept at  $25^{\circ}$ , and all the usual precautions were taken to make the observations as accurate as possible. The conductivity of solutions of thalious chloride and thalious bromide were first measured. The limit of solubility of thalious bromide at  $25^{\circ}$  is at about one molecular weight in 250 liters, so that the first observation in the case of the latter salt is of doubtful value.  $\mu^1$  and  $\mu^2$  are calculated from measurements of two separate and independent solutions :

v.	TlCl.		TlBr.	
	$\mu^1$ .	$\mu^2$ .	$\mu^1$ .	$\mu^2$ .
62.5	128.5	129.1	....	....
125	133.9	133.9	....	....
250	136.8	137.1	132.3(?)	137.0(?)
500	139.4	139.3	147.0	148.4
1000	145.5	143.2	149.2	150.0
2000	146.2	145.0	150.1	151.0

The solution of thallous bromide at the dilution 250 was now oxidized with pure bromine and 100 cc. of this oxidized solution boiled until all excess of bromine was driven off. The solution was made up to 100 cc. again with pure water, and the conductivity measured. The fact that hydrolysis had taken place was shown by a very slight brownish tinge of the solution and a faint acid reaction to indicators. The results, however, are none the less interesting. From the figures tabulated below we see that on oxidizing thallous bromide to thallic bromide the conductivity drops to a surprising extent, especially when the calculations are based on the reaction,



v.	Taken as $\text{TlBr}_3$ .	Taken as $(\text{Tl}'''\text{Br}_6)\text{Tl}''$ .
	$\mu$ .	$\mu$ .
250	61.6	123.2
500	78.8	157.6
1000	103.6	207.2
2000	141.3	282.6

As part of the observed conductivity is due to the slight amount of hydrobromic acid formed by hydrolysis, we have to conclude, on the basis of the first assumption, that  $\text{TlBr}_3$  is very slightly dissociated, if at all. On the other hand, when the calculation is based on the double formula, under Werner's theory we have two trivalent ions,  $(\text{Tl}'''\text{Br}_6)^-$  and  $\text{Tl}'''^+$ .

After each dilution more hydrolysis takes place and the minimum tone in the telephone receiver requires a constant move to the right of the sliding contact on the bridge wire. A constant position is, however, soon reached for each dilution. It was noticed in the course of this investigation that the solution of thallic bromide, after an interval of several weeks, during which it had stood in a glass-stoppered flask in the laboratory, had a much smaller conductivity than when first measured. This change was accompanied by an almost complete disappearance of the acidity as shown by indicators. The results are given in the following table :



v.	TlBr <sub>3</sub> (at once).	TlBr <sub>3</sub> after three weeks.	TlBr <sub>3</sub> after eight weeks.
	μ.	μ.	μ.
250	61.6	46.2	46.7
500	78.8	53.9	54.2
1000	103.6	64.7	65.1
2000	141.3	92.6	92.7

The reason for this change is not quite clear and is worthy of further investigation. It is possible that the hydrobromic acid under the influence of light, may be oxidized, but in that case it is hard to understand why further hydrolysis does not take place. The thalious chloride solution was oxidized with bromine in the same way as the thalious bromide, with the following results:

v.	Taken as TlClBr <sub>2</sub> .	Taken as (Tl <sup>III</sup> Cl <sub>2</sub> Br <sub>4</sub> ) Tl <sup>I</sup> .
	μ.	μ.
250	71.1	142.2
500	104.0	208.0
1000	136.2	272.4
2000	188.2	376.4

### Conclusion.

In summing up the evidence so far collected on the constitution of these double salts, it must be admitted that the question is still unsettled. The fact that these compounds are manifestly and easily dissociated into thalious and thallic compounds by heating in their own mother-liquors as described, would seem to argue against the theory of Werner. Again, the fact that silver nitrate produces immediate and complete precipitation in the cold, and that platinic chloride forms with them precipitates of thallium chloroplatinate, the thallic portion remaining in solution, points in the same direction. On the other hand, as has been stated, some of the evidence would seem to point in the other direction. The results of the conductivity measurements, as far as they have gone, appear to find a more rational explanation under the theory of Werner than under the old linkage theory. Finally, it may once more be pointed out that if TlBr<sub>3</sub> and TlCl<sub>3</sub> exist, and are even to the slightest degree dissociated in solution, there is no reason why the isomeric compounds TlBr<sub>3</sub>·3TlCl

and  $\text{TlCl}_3 \cdot 3\text{TlBr}$  should preserve their identity through successive crystallizations.

In concluding this first paper on this subject the author wishes to express his indebtedness to his colleague, Dr. E. P. Kohler, for many valuable suggestions. For the large amount of material from which the thallium was obtained the author has to thank Hamilton Emmons, Esq., of Leamington, England.

May 15, 1900.

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## A MULTIPLE FAT EXTRACTOR.

BY CHARLES L. PENNY.

The chief object of the device and method described below is so to expedite the determination of fat in milk and its products as to make accurate gravimetric determinations economically possible in competition with the speedy volumetric methods now in use. This could hardly be accomplished if it were required to determine fat gravimetrically within the few minutes that the latter methods require. But when many samples are to be analyzed, if a large enough number may be worked simultaneously, the average time for each may be very short. This, then, is what is attempted; *viz.*, to extract almost any number of samples at the same time and in a single piece of apparatus, with only so much individual time spent on each as may suffice to measure the substance and to weigh the product.

The apparatus devised to this end differs in its principle of action little, if at all, from the well-known Soxhlet extractor. Its sole peculiarity is such an arrangement of parts as admits any number of samples at the same time and under a single operation to the action of the same extracting liquid. This is attained by the use of a single common chamber for all of the samples, in which they are held in shallow capsules placed parallel and close together. This chamber consists of a brass cylinder two and one-half inches in diameter and of such length as the number of simultaneous extractions may require; each half inch in length, approximately, admits a separate sample. The form described below is thirty inches long and

admits simultaneously fifty-one samples. The weight of the extract is determined by difference.

Besides the cylinder which contains the samples there are needed devices for vaporizing the extracting liquid, for condensing it and returning it condensed to the cylinder, and for siphoning from the cylinder, after the manner of the common siphon extractors. The only complication of parts beyond those used with simple extractors is caused by the large quantity of extractive liquid needed for work on a large scale. The cylinder just described contains about 2400 cc. ; to vaporize and condense speedily this quantity of liquid requires not only much larger parts in the apparatus but also a more complicated arrangement of them.

Fig. 1 shows the essential parts of the apparatus and their arrangement : a complete front view on the left and a partial side view on the right. The chamber or cylinder which contains the samples is shown at C ; the boiler at B, in this case fitted with steam coils at S to obviate the use of flame with so large a quantity of inflammable liquid ; the condensing coils are shown above at L and Y, their surrounding water jackets being omitted from the sketch ; each has a separate water jacket, that of the smaller coil which is really placed inside of the larger, receives the cold water first. The vapor of the extracting liquid passes from the boiler by the tube N upward into the large coil, by which it is condensed ; a portion of the condensation returns reflux into the annular space between the outer tube D and the inner tube I ; the remaining portion, frequently the greater, is blown by the force of the incoming vapor over into the small coil from which it returns downward through G into the annular space just mentioned. Communication with the external air is at V ; the vessel A allows the air to escape without the expulsion of the liquid with it. Doubtless a single large ball condenser might serve the purpose of the two coils here used, but with a coil it was found impossible to return all of the condensation reflux against the large quantity of ascending vapor. The condensations having returned to the annular space are heated by the ascending vapor in the inner tube I and, thus heated, flow through F into the cylinder C at its front end,

next to W in the side view. The siphon tube leaves the cylinder at the opposite end next to T, and passing underneath the length of the cylinder returns to the boiler as shown. The cylinder is not quite horizontal, the end T being a trifle lower. Equal vapor-pressure in boiler and cylinder, without

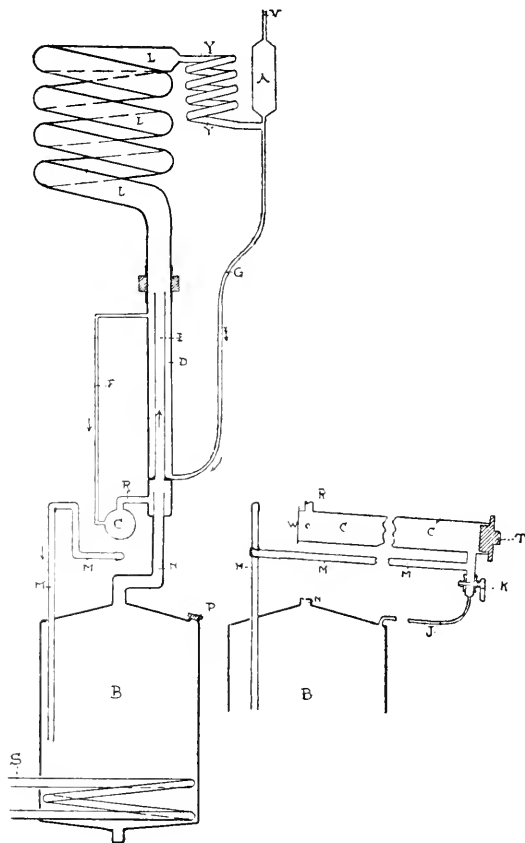


Fig. 1.

which the siphon would not work, is secured through the tube R as shown. During the extraction the cock K remains closed; afterward and previously to the removal of the cap T the former is opened to drain the liquid back into the boiler. The front of the cylinder at W is closed with mica to allow the operator to watch the process; the opposite end is closed

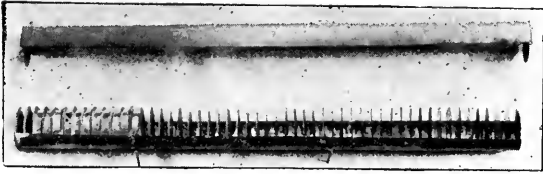


Fig. 2.



with a screw cap fitted with a leathern gasket. The parts of the apparatus are copper and brass, except the coils which are of lead for the steam, and block-tin for the condensers.

The samples to be extracted, which for the present may be supposed to be either milk, cream, skim-milk or butter, are treated after the general method of difference analysis. About 5 grams of the substance is weighed or measured into a tin-foil capsule two inches in diameter and three-eighths of an inch deep; such as are used for capping salt-mouth bottles serve admirably and are so cheap that they may with economy be thrown away after a single use. These capsules are previously charged with an absorbent such as sand or asbestos. If, in the case of milk analyses, total solids are desired, the capsule with the absorbent must, of course, be weighed previously to the addition of the milk; if the fat only is desired, this weighing is unnecessary.

The capsules with their samples are dried in the usual way and weighed. Thus the substance ready for extraction is in the form of a disk two inches in diameter and about three-sixteenths of an inch thick, securely adherent to the tin capsule but, on account of its thin cross-section, well exposed to the action of the extracting liquid and, with a proper absorbent, exceedingly permeable. The capsules are then placed in the semicircular rack shown in Fig. 2, and covered with the loose-fitting semicircular cover also shown. The rack is introduced into the cylinder of the extractor so that the crevices between the rack and its cover are in the vertical plane, an arrangement that permits the extracting liquid to surround the capsules, and to be drained off completely by the siphon action. After the cylinder is closed with the screw cap, and the cock, K, Fig. 1, also closed, the extraction is started by the admission of steam to the steam-coils at the bottom of the boiler, or by the application of some other source of heat. When the extraction is complete, the heat is shut off, the cock K is opened, and the capsules are removed. The latter are dried again and weighed, the difference being the fat.

As to the choice of absorbents, in the case of whole milk or skim-milk, in some respects asbestos is preferable, in others

coarse sand. The asbestos is much lighter and much more quickly weighed, but it is also hygroscopic. If total solids are to be determined, the capsules containing asbestos require previous drying, and weighing from desiccators. Sand, while it is heavier and slower in the weighing, is of constant weight in the air. The tin capsules mentioned above, two inches by three-eighths, weigh on an average about 7 grams. To absorb properly 5 cc. of milk, from 12 to 14 grams of sand are required while hardly more than 2 or 3 grams of asbestos. In the case of cream, and, of course, in the case of butter, sand can not possibly be used; something fibrous like asbestos is necessary in order that it may remain in the capsule. Fine powders, like precipitated carbonate of lime, are almost impervious to the extracting liquid, while asbestos, and, still more, coarse sand leave little to be desired in this respect. Paper such as is used in the Adams method would be an excellent absorbent, but doubtless its hygroscopic quality and inconstancy in weight would make it impracticable for a difference method. Glass-wool can be made to serve as a good absorbent, but it is both expensive and difficult to fit properly into the capsules on account of its elasticity. Coarse sand is the easiest to prepare and the cheapest; in proper proportion to the milk it is as satisfactory as anything that could be used.

As the capsules are placed in the extractor with their axes parallel to that of the cylinder, in other words as they stand almost vertically on edge, without a covering of filter-paper, it is clear that nothing loose enough to fall out, and so to be lost, is admissible. Sand in the proportion of about two and one-half times the weight of milk forms a firm, compact cake with the dried milk, such as admits of inversion of the capsule without the slightest chance of loss. Too much sand, of course, might leave some loose grains that would be washed away by the solvent, and thus incorrect results would be obtained. This question, however, in practice causes no difficulty whatever in the use of sand; if it be roughly measured into the capsules, a perfectly firm cake is obtained that will, with proper treatment, lose nothing mechanically during the extraction. Out of hundreds of tests with sand



there has never been a trace of mechanical loss, except where the sand cake was accidentally broken by an ill-fitting rack. Such cases, of course, would be instantly recognized and, with a proper size of rack and capsule, would never occur. Cream (and, of course, still more butter) forms too friable a cake to bind the sand, hence for such samples a fibrous absorbent, like asbestos or glass-wool, must be used. Asbestos forms with milk so firm a mat that the capsule may be dropped upon the floor and deeply indented without a particle of loss in weight. In fact very fair results may be had without any absorbent. If the milk, not more than 5 cc., be dried in the capsule without an absorbent, it may be extracted with very little danger of loss and with a fair degree of accuracy, though the extraction may be slower and a trifle less complete. Milk thus dried forms a rather brittle shell or hard skin that might well be expected to suffer certain loss from the mechanical action of the extracting liquid; yet with but ordinary care this loss does not occur, so that it would be entirely possible, though perhaps not advisable, to dispense with all absorbents.

For the purpose of milk analysis "petroleum ether" seems to have decided chemical advantages over ether, aside from its relatively low cost. The "petroleum ether" will boil at a considerably higher temperature than ether, and this, if it is below  $100^{\circ}$ , must be considered an advantage. The temperature of the interior of the boiler usually varies from  $75^{\circ}$  to  $85^{\circ}$  C. and the cylinder containing the samples is a few degrees cooler. The high temperature at which the solvent acts must hasten considerably its action. This, combined with the remarkable penetrating power of petroleum, makes it a solvent of the greatest efficiency. The time of complete extraction when sand is used as an absorbent may be in some cases as short as an hour, though usually a longer time is required. With asbestos several hours are usually necessary. As a large number of samples may be worked at one time, there is no object in unduly hastening the extraction; after six hours, however, it may be regarded as complete and, as this work may easily be effected during the night by means of a steam-heating plant, the particular duration is of little moment.

Suffice it to say, that probably after six hours the most prolonged extraction would fail to remove anything. In view of the fact that fifty, or with quite practicable arrangements, a hundred or more extractions might be made simultaneously, it would seem that the time of making a single gravimetric determination of fat is but little more than is required to make two weighings. Where the total solids of milk are determined a single additional weighing gives the fat. The time spent in drying and extracting may seem to be considerable if only a few samples are to be analyzed, but with large numbers this time is greatly reduced, and the automatic action of the device leaves the analyst free except during the transfer and weighing of his samples.

"Petroleum ether" as a partitive solvent seems to be far sharper in its lines of division than ether. It is well known that it is difficult to extract with ether to the point of an absolutely insoluble residue. Even blank trials of an ether-extracting apparatus that is fitted with corks usually show something soluble at each repetition. On the contrary, the milk residues, after a few hours' extraction with "petroleum ether," failed to lose anything appreciable by subsequent extraction. In other words, the division between "petroleum extract" and the residue is much more exact than in the case of "ether extract." This fact is probably due chiefly if not wholly to the great difficulty in drying ether and in keeping it dry, and also in drying the substance to be extracted. Only with extreme precaution can absolutely dry ether and an absolutely dry substance (for the latter is indispensable to the former) be maintained. "Petroleum ether," on the other hand, seems to be unaffected by moisture. Capsules containing extracted milk residues were treated with from 0.17 to 0.18 gram of water and thus moist were extracted without appreciable loss of weight; they were furthermore exposed to the open air on a damp day for a number of hours, and thus extracted without any appreciable change in the dry weight. The objection usually made to "petroleum ether" that it is not of definite composition would seem to apply with even more force to ether, which, as it is generally used, is itself a mixture of ether with a small but variable amount of water;

especially is this of moment in the extraction of milk and its products, which contain so much non-fatty matter that is soluble in slightly aqueous ether.

In the work with this extraction apparatus, the lighter portion of "stove gasoline" was used in place of the more costly "petroleum spirit" as it is called. The gasoline gives off at steam heat about one-half of its volume, the heavier residue remaining behind useless for this purpose. Yet with the loss of one-half, it forms one of the cheapest reagents that can be used,—so cheap in fact that the question of cost may be left out of consideration. The results obtained by the use of this extractor compare favorably with those by the ether-sand method, and in point of concordance the former have an advantage. With a large number of repetitions the multiple extractor gives less fluctuation than the ether-sand method.

While the original application of this device was to milk and its products, it seems to promise good results and expedience in fat-estimation in other substances.

DELAWARE COLLEGE

AGRICULTURAL EXPERIMENT STATION, June, 1900.

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## ADLUMIA CIRRHOSA—A NEW PROTOPINE-BEARING PLANT.

BY J. O. SCHLOTTERBECK.

*Adlumia cirrhosa*, which is variously known as Alleghany Vine, Mountain Fringe, and Climbing Fumitory, is a delicate vine climbing by its slender young leaf stalks over high bushes in wet woods, from New England to Michigan, Eastern Kansas and southward. It is also largely cultivated in gardens because of its beautiful, finely-cut foliage. It is a member of De Candolle's *Fumariaceæ*, a family so closely related to the *Papaveraceæ* that modern systematists have agreed that it more properly occupies the position of a tribe of the latter family.

Since all plants of the *Papaveraceæ*, as far as they have been studied, are alkaloid-bearing, one would be reasonably safe in assuming that all other plants of this family contain one or more alkaloids. Indeed, it would seem strange if we should

encounter a plant of this family that would fail to respond liberally to the tests for alkaloids. This process of reasoning led me to take up the chemical study of the above-named plant.

For this investigation the plant, which is a biennial, was collected in the fall of the first year's growth from the botanical garden of the University of Michigan. The roots were dug, washed, separated from the leaves and stems, and carefully dried with the aid of artificial heat. Of the thoroughly dried root, which was ground to a No. 40 powder, 10 grams were macerated twenty-four hours in a closed flask, with 100 cc. modified Prollius fluid. About 10 cc. of the filtered fluid were then evaporated to dryness on the water-bath, and the residue taken up with several small portions of water acidulated with acetic acid. The filtrate gave abundant precipitates with Mayer's and Wagner's reagent, and with ammonia water, thus indicating the presence of alkaloids. The approximate yield was estimated gravimetrically with 25 cc. of the Prollius extract, and was found to be about 1 per cent. The leaves contained very much less.

In order to learn more of the properties of the alkaloidal substance, 100 grams of the powdered root were thoroughly moistened with ammonia water, to liberate the alkaloids from their combinations, then carefully and thoroughly dried in a current of warm air, and completely exhausted in a Soxhlet apparatus with chloroform. The percolate was subjected to distillation for the recovery of the chloroform, and the residue treated with several portions of water acidulated with acetic acid. This was done upon the water-bath in order to insure the complete extraction of the alkaloid, which is more or less mechanically held by the sticky residue. The combined extracts were cooled, filtered, placed in a separatory funnel, and made alkaline with ammonia water. A voluminous, almost white, precipitate, which assumed the character of a curd, was thrown out. This was shaken with ether, whereupon the precipitate at once went into solution. This solution was only temporary, however, for from the filtered ether solution the alkaloid began to separate almost immediately in the form of white warts or sphæro-crystals, and in a few minutes practically all of the alkaloid had separated.

For the purpose of purification the alkaloid was taken up with dilute acetic acid, reprecipitated with ammonia water, shaken with ether, rapidly separated and filtered, and set aside to crystallize. This operation was repeated until a practically constant melting-point was obtained. After recrystallizing several times, finally from acetic ether, a melting-point of  $203^{\circ}$ (uncorr.)– $207^{\circ}$ (corr.) was obtained.

This alkaloid is very insoluble in petroleum ether, practically insoluble in water and in absolute alcohol, and but slightly soluble in ether, when it is in the crystalline state. When freshly precipitated from solutions of its salts by means of ammonia water, however, it is, as shown above, temporarily very soluble in ether. Its best solvent is chloroform. Being but very slightly soluble in absolute alcohol and very soluble in chloroform, a mixture of these forms an excellent medium from which the alkaloid may be easily obtained in beautiful prismatic crystals. It possesses the peculiar property of crystallizing in two different forms; *viz.*, in warts or in single prisms of the monoclinic system. Depending usually upon change of solvents, one crystalline form can be converted into the other. Even from the same solvent as from ether, or from alcohol, both forms are produced simultaneously.

The chloroplatinate forms dark-yellow sphæro-crystals while the chloroaurate forms tufts of needle-like crystals. Concentrated sulphuric acid gives momentarily with a small quantity of the alkaloid a red color, but this is immediately followed by a deep violet. Concentrated nitric acid dissolves it in the cold without color but, upon warming, it becomes red. Erdmann's reagent turns it deep violet-blue at once.

Although sufficient quantity of the alkaloid was not at hand to make combustions, enough of its properties have been determined to make its positive identification possible. In its crystalline form, solubility in the crystalline and freshly precipitated states, melting-point, color reactions, and crystalline forms of its chloride, sulphate, chloroplatinate, and chloroaurate, it agrees exactly with the protopine which we have separated from *Bocconia cordata*,<sup>1</sup> and with a specimen of protopine from opium.

<sup>1</sup> Merrill and Schlotterbeck : Proc. A. Ph. A., 1900.

The formula as determined by Hesse<sup>1</sup> and by Eijkman<sup>2</sup> is  $C_{20}H_{19}NO_5$ . Selle,<sup>3</sup> and Koenig and Dietz<sup>4</sup> obtained results which agree better with the formula  $C_{20}H_{17}NO_5$ . In spite of this small discrepancy, which is likely to occur with different operators, we are justified in asserting that the alkaloid which these investigators have investigated is in each case protopine. The conclusion as to the identity of the alkaloid of *Adlumia cirrhosa* is based upon the very characteristic properties above mentioned and upon the fact that it is identical with the protopine which we have separated from *Bocconia cordata*.

While collecting the literature upon this subject the striking similarity of the physical properties of protopine, which is the most frequently occurring alkaloid in the *Papaveraceæ*, with those of fumarine, which is the alkaloid of most frequent occurrence in the *Fumariaceæ*, was noticed. An excellent opportunity for comparing these two bodies was offered in the study of *Bocconia* and *Adlumia* which was going on in this laboratory at the same time. A specimen of fumarine, separated from *Fumaria officinalis* by P. F. Trowbridge, was also kindly placed at the disposal of the writer for additional comparative study. The composition of the alkaloid from two of these sources was not determined because of scarcity of material, but in physical properties they agreed in every particular. Fumarine is therefore probably identical with protopine.

Protopine has been found in *Papaver somniferum*,<sup>5</sup> *Bocconia cordata*,<sup>6</sup> *Chelidonium majus*,<sup>7</sup> *Escholtzia californica*,<sup>8</sup> *Sanguinaria canadensis*,<sup>9</sup> *Stylophorum diphyllum*,<sup>10</sup> and *Adlumia cirrhosa*.

Fumarine has been reported in *Fumaria officinalis* at different times by Peschier,<sup>11</sup> Hannon,<sup>12</sup> Preuss,<sup>13</sup> and Reichwald.<sup>14</sup> Battandier<sup>15</sup> found it in *Glaucium corniculatum* and in six or

<sup>1</sup> Ann. Chem. (Liebig), Suppl., 8, 318.      <sup>2</sup> Rec. Trav. Chim., 3, 182.

<sup>3</sup> Arch. Pharm., 228, 441.

<sup>4</sup> Ibid., 231, 145.

<sup>5</sup> Hesse : Ann. Chem. (Liebig), Suppl., 8, 318.

<sup>6</sup> Eijkman : Rec. Trav. Chim., 3, 182 ; Pharm. J. Trans. [3], 13, 87 ; Murrill and Schlotterbeck : Proc. A. Ph. A., 1900.

<sup>7</sup> Selle : Arch. Pharm., 228, 441.

<sup>8</sup> Dankwortt : Inaug. Dissert., Erlangen, 1890.

<sup>9</sup> Koenig and Dietz : Arch. Pharm., 231, 145.

<sup>10</sup> Selle : Arch. Pharm., 228, 96.

<sup>11</sup> Jsbr. Fortschr. physik. Wiss., 1832, 245.

<sup>12</sup> Ibid., 1852, 550.

<sup>13</sup> Ztschr. Chem. (1866), 2, 414.

<sup>14</sup> Russ. Ztschr. Pharm., 28, 161.

<sup>15</sup> Compt. rend., 114, 1122 ; 120, 1276.

more genera of the *Fumariaceæ*. Later he isolated it from *Bocconia frutescens*.

Since fumarine was discovered and named long before its discovery in opium by Hesse, it is but proper that the name protopine be dropped.

From the above it is seen that the alkaloid in question occurs in a greater number of plants than any other known alkaloid.

SCHOOL OF PHARMACY,  
ANN ARBOR, MICH.

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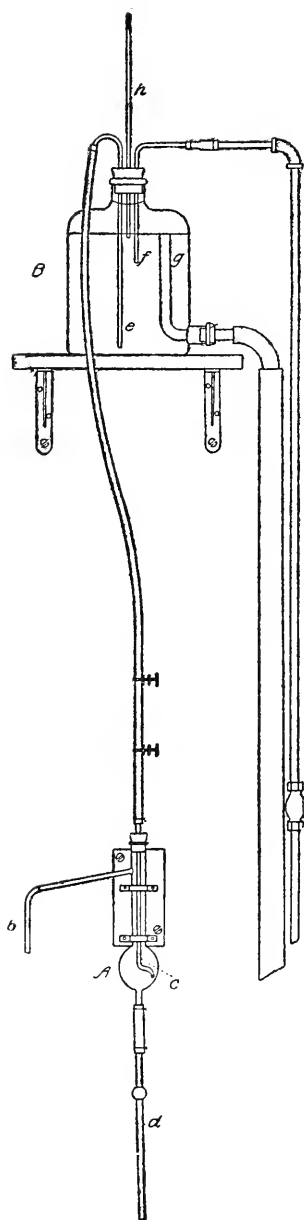
## A MODIFICATION OF THE BUNSEN VACUUM-PUMP.

BY MARTIN H. ITTNER.

The laboratory vacuum-pump about to be described will, under certain conditions, be found to possess merit over the regular form of water-pump devised by Bunsen. Where there are several faucets on the same line of pipe which supplies a Bunsen pump, as is frequently the case, the flow of water through the pump is liable to fluctuate. There is a certain flow of water which produces the maximum efficiency, and when, for any reason, there is a change in the flow it is a common occurrence for some water to be drawn back into the vessel that is being exhausted. This is always annoying, and especially so when the volume of water thus sucked back is sufficient to fill the empty bottle usually placed between the vessel to be exhausted and the vacuum-pump.

Frequently, the water entering the pump contains bubbles of air which, coming at irregular intervals, cause more or less variation in the pressure within the vessel being exhausted.

The illustration shows a pump free from the most serious objections met with in the use of the Bunsen pump. It can readily be fitted up in any laboratory where a sufficient fall to the run-off water can be had. A Wurtz distilling column, *A*, 8 inches long, is selected, having an inner diameter of about 8 mm. to the tube at the bottom. A glass tube *c*, about 6 mm. in diameter and 10 inches long, is bent at one end for a short distance in the form of a helix. The opening at the end of the helix is about 3 mm. in diameter. This tube is pushed



through a singly perforated soft rubber stopper which fits the large opening of the tube *A*. The upper end of the inner glass tube is enlarged slightly so as to fit rubber connections better. The lower end of the tube *A* is connected by means of a stout piece of rubber tubing with the lead run-off pipe *d*, whose inner diameter is about 8 mm. ( $\frac{5}{16}$  of an inch), the upper end of which is soldered to a short length of brass pipe having the same internal diameter. The lower end of *d* is about 37 feet below *A* and has a slight S-bend before connecting with the sewer. An iron pipe, with its unions and connections, cannot be used if a good vacuum is to be obtained.

A 4-liter aspirating bottle, *B*, is placed on a shelf about 3 feet above the bottom of the tube *A*. The upper opening of this bottle is fitted with a stopper having three perforations, through which pass the siphon tube *e*, the water feed-tube *f*, and the tube *h*. The lower opening to the bottle is fitted with a stopper through which passes the large curved overflow-tube *g*, ending within the bottle near the top. The stopper holding this tube is wired to the neck of the bottle as a precaution. The tube *h*, open at both ends, has its lower end



just below the upper end of the overflow-tube *g*. The feed-tube *f* ends about an inch below *h*. The siphon-tube *e* reaches nearly to the bottom of the bottle at one end, while the other end is connected with a rubber tube through which water may flow, passing through *c* and *d*.

When the pump is in use water is allowed to enter the bottle from the water-supply pipe *f* at such a rate that there will always be a slight overflow through *g*. All air not dissolved in the water rises to the surface and passes out of the overflow *g*. Water from the bottom of the bottle passes through *e*, and the flow may be regulated by two screw-clamps on the rubber connection. The lower of these clamps is set at the position which is found to give the most efficient flow of water and is always left there; the upper one is closed when the pump is not in use, and opened wide when in use. The water issuing at the lower end of *e* in a direction tangential to the helical end of *e* imparts a rapid rotary motion to the water in the bulb at the lower part of *A*. Whether the flow of water is slow or fast, this rotary motion always forms a vortex which carries air down the tube *d* with great rapidity. The side tube *b* is connected with the vessel to be exhausted. A volume of air equal to 1 liter can be exhausted in a few minutes until the pressure is less than 20 mm. of mercury. After the water flowing through the bottle *B* has assumed a constant temperature the vacuum remains almost perfectly constant, it being only necessary after starting the pump to see that the supply of water entering through *f* is always a little greater than that passing through *c*. The water passing through *A* does not come near the tube *b*, and there is no chance whatever of its entering *b* if the bottle *B* is kept full of water, and if ordinary care is used.

The apparatus has been found especially well adapted to distillation *in vacuo*, as a very good vacuum is easily obtained and maintained throughout the whole process with scarcely a perceptible variation in the pressure indicated by the manometer.

JERSEY CITY, May 2, 1900.

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# A NEW VOLUMETRIC METHOD FOR THE DETERMINATION OF SILVER.<sup>1</sup>

BY LAUNCELOT W. ANDREWS.

The chief volumetric methods now in use for silver determinations are those of Gay Lussac,<sup>2</sup> Pisani,<sup>3</sup> Mohr<sup>4</sup> and Volhard.<sup>5</sup>

Of these, the first, as is well known, is a process of great accuracy, applicable to acid solutions, but is tedious in execution. The second and third are only to be used in perfectly neutral solutions so that their application is extremely limited, being excluded in those cases where neutralization produces a precipitate. The method of Volhard is free from these drawbacks but is seriously interfered with by the presence of substances which impart a yellow or red color (such as cobalt salts) to the solution and for those cases in which the amount of silver is extremely small or the solution highly dilute, it lacks the sensitiveness of the methods of Gay Lussac or Pisani, probably because the reaction between sulphocyanates and ferric salts is less delicate as a test for the former than for the latter.

It has therefore appeared to the author to be a matter of some interest to devise a method applicable to acid solutions containing silver along with a variety of other metals, possessing the delicacy characteristic of the starch-iodide reaction. It is the purpose of this paper to present such a method, based upon that of Pisani.

In Pisani's method, a solution of starch iodide is run into the silver solution containing calcium carbonate in suspension.

The exact nature of the reaction which then occurs and which culminates in decolorization of the iodide of starch has not been as yet cleared up in spite of several investigations which have been published on the subject. Silver iodide is precipitated along with oxidized products, silver

<sup>1</sup> Presented at the New York meeting of the American Association for the Advancement of Science, June 28, 1900.

<sup>2</sup> G. J. Mulder: *Scheikundige verhandelingen*, 1857.

<sup>3</sup> *Ann. des Mines* [5], 10-83.

<sup>4</sup> *Titrimethode*, 3rd ed., § 151.

<sup>5</sup> *Ann. Chem. (Liebig)*, 190, 1.

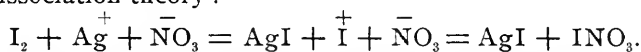
iodate, hypiodite or, possibly, silver peroxide in the latter stages of the reaction. Strict proportionality does not exist between the amount of starch iodide consumed and the silver present, although such proportionality is more nearly approached as the solution used is more dilute. The departure from proportionality for solutions between  $\frac{N}{100}$  and  $\frac{N}{200}$  is considerable, as the following experiments show.

In each experiment 25 cc. of a solution containing 0.7887 mg. of silver <sup>per c.c.</sup> was employed and the quantity of water added was varied. The results of one set of observations are subjoined.

Expt. No.	Vol. of water added in cc.	Vol. of Pisani's sol. required. cc.	Character of end reaction.
41	None	15.70	Obscure, color dirty.
42	300	18.60	Sharper.
43	None	15.40	As in No. 41.
44	500	20.25	{ Sharp. Change from brownish to blue.
45	300	18.70	As in No. 42.

If the effort is made to titrate a silver solution acidified with nitric acid by one of starch iodide, a series of colors may be observed, beginning with yellow and passing through orange, brown, gray, sage-green, etc., without any turning point being clearly marked.

During these changes, the solution exhibits powerfully oxidizing properties, more marked than are shown by dilute solutions of either iodine or of iodic acid. The reaction between free iodine and solutions of silver nitrate is now under investigation at this laboratory, and the author hopes to publish definite results before long; in the meantime it will suffice to say that the following general reaction is probable, the equation being written in the sense of the electrolytic dissociation theory:

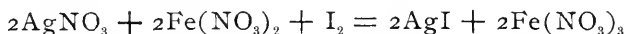


Here the iodine plays a part similar to that which it holds in iodine monochloride and the—for the present—hypothetical compound  $INO_3$  is to be regarded as the carrier of the oxidizing properties referred to above. It exerts the oxidizing action upon organic matter present (as starch) and upon any

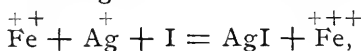
other reducing substances such as ferrous salts, nitrous acid, or tetrathionates. It undergoes, in part, hydrolysis into HOI and nitric acid and, in part, reacts with the excess of silver nitrate, producing a reddish-brown solution precisely similar in appearance and properties to that obtained by dissolving "silver peroxide" in nitric acid,<sup>1</sup> and which presumably contains silver pernitrate.

In place of these complicated reactions, a simple one ensues if from the start a sufficient quantity of a feeble reducing agent is present, as ferrous salt or nitrous acid, of such character as not to react with free iodine or starch iodide. In that case a smaller quantity of the solution of iodide of starch will be required than if the titration were conducted according to Pisani in neutral solution, and the end of the reaction is marked by a sharp change from pale yellow to blue.

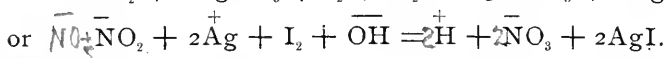
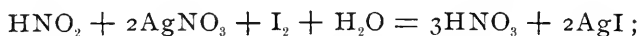
The reaction is shown by the equation :



or more simply according to the dissociation theory :



and, for the case in which nitrous acid is present, by



As might be expected from the respective equations, the reaction in the presence of ferrous salts is practically instantaneous, while that which takes place in the presence of nitrous acid is much slower, especially in very dilute solutions, owing to the slight dissociation of the water and consequent small number of hydroxyl ions that are directly involved in the reaction.

Dilute solutions of ferrous salts, slightly acidified by strong acids will very slowly decolorize properly prepared starch iodide, with the formation of traces of ferric salts. This action can be checked by the previous addition of ferric salt. Thus, if 2 cc. of a solution of forty grams of crystallized ferrous ammonium sulphate in a liter of water be added to 100 cc. of

<sup>1</sup> J. Fischer: J. prakt. Chem., 33, 237.

see errata 125 p. 514

water containing 5 cc. of dilute nitric acid, and a few drops of N/1000 starch iodide then run in to color the liquid blue, spontaneous bleaching will ensue in about five minutes, whereas, if the iron solution also contains 40 grams of ferric ammonium sulphate (cryst.) per liter, five to eight hours will elapse before the blue disappears. That there is a condition of equilibrium between ferrous and ferric salts and iodine and iodide has been shown by Seubert and <sup>Banner</sup> and by Seubert and Rohrer.<sup>2</sup> *see errata 1.25p 518*

In applying the facts just set forth to the development of a practical volumetric method, the slight solubility of silver sulphate must be born in mind. If the iron sulphate is added to a too concentrated silver solution and then titration with starch iodide is undertaken, silver sulphate will be thrown down with silver iodide and partly enveloped by the latter, making the end-point obscure and the results more or less inaccurate. Some of the experiments described in the following pages give evidence of this fact and also show the permissible limits of concentration.

Before describing in detail the analytical method, it will be well to say a word regarding the adjustment of apparatus and the preparation of solutions employed.

#### *Apparatus.*

All burettes and other pieces of volumetric apparatus employed in the work were carefully calibrated and the readings corrected to true cubic centimeters. The burettes were divided into 1/10 cc. with divisions sufficiently wide to permit 1/100 cc. to be estimated with an error of not more than 2/100 cc. The solution of iodide of starch in the concentrations used is almost perfectly opaque and permits very exact readings to be taken from the top of the meniscus, which method was uniformly used.<sup>3</sup> Pipettes and burettes were

<sup>1</sup> Ztschr. anorg. Chem., 5, 339-411.

<sup>2</sup> Loc. cit., 7, 137.

<sup>3</sup> The use of a float is not to be recommended, according to the author's experience, for either opaque or transparent liquids. Many series of readings made with and without this device, the results being controlled by weighing the liquid delivered, have shown that the float increases instead of diminishing the probable error of a reading, provided the readings are taken in the proper way when no float is used; i. e., with suitable illumination.

frequently cleaned with a strongly alkaline solution of potassium permanganate followed by hydrochloric acid, a method to be recommended in preference to that involving the use of sulphuric acid and potassium bichromate commonly employed.

*Preparation of Standard N/10 Silver Solution.*

Commercial "pure silver 1000 fine" was dissolved in pure nitric acid and water, heated in porcelain and filtered. An excess of the purest hydrochloric acid was added and stirring continued until the precipitated chloride had become granular. The precipitate after being thoroughly washed by decantation was reduced by digestion on the steam-bath with formaldehyde and ammonia. The silver sponge so obtained was washed with distilled water, compressed and fused in an unglazed porcelain crucible without flux, cast in an ingot mold, treated with fusing caustic potash, and finally cleaned mechanically. The N/10 solution was made up to contain 10.793 grams (corrected) of this silver per true liter. From this standard a N/100 solution was prepared directly by dilution, and for some of the experiments, other, less pure, silver solutions were standardized by comparison.

*Preparation of the Starch Iodide.*

The best obtainable commercial maize starch was repeatedly washed with water by decantation, strained through linen, washed with dilute hydrochloric acid, then with pure dilute caustic potash, again with hydrochloric acid, then in turn, with water, alcohol, ether, and finally alcohol, and dried at 40°. This purification is not essential, but the starch employed had been purified in this way for the purposes of a correlated research on the properties of starch iodide.

Of the prepared starch, 50 grams were ground dry with 8 or 9 grams of resublimed iodine until well incorporated and the powder stirred with 100 cc. of distilled water, sealed up in large glass tubes and heated for several hours in boiling water. Instead of heating in sealed tubes, boiling with water in a flask with reflux condenser may be equally well employed, the iodine, which at first sublimes into the condenser, being

pushed back into the liquid from time to time. The substance obtained in either way, after moderate dilution, is filtered through a "toughened" (parchmentized) filter. Solution is complete. N/20 standard solutions were made, but N/100 is as far as it is convenient to go in concentration usually. These solutions are as absolutely permanent as any volumetric solutions can be, changing in strength only by evaporation of water. By blowing a current of air through such a solution for a day or two the vapor-pressure of the iodine can be reduced to 0.005 mm., and even less, as was determined by a method to be published elsewhere.

For all titrations where an iodine solution weaker than N/20 is to be used, as in the titration of alkaline arsenites, antimonous salts, etc., iodide of starch solutions are to be preferred to those prepared in the ordinary way from potassium iodide and iodine, since the former are more permanent, give an even sharper end reaction, can be more exactly read off in the burette and avoid the difficulty of preparing a clear, permanent starch solution as indicator or the trouble of always making up a fresh one. The standard of a solution of starch iodide as regards silver is not the same as its standard toward sodium thiosulphate, since only a part (often about  $\frac{2}{3}$ ) of its iodine is in a condition to react with reducing agents, the remainder being in a form analogous to an alkyl iodide, reactive toward silver salts but not toward thiosulphates, and the like.<sup>1</sup> In some experiments (referred to below) a N/10 solution was prepared (designated "Sol. A") by mixing about 600 cc. of N/50 starch iodide with about 400 cc. of ordinary decinormal iodine solution. The mixture was decinormal as regards total iodine. Such solutions can be used when larger amounts of silver are to be titrated, but I believe it to be better in such cases to precipitate the greater part of the silver with a N/10 potassium iodide solution and finish with the N/100 starch iodide, or to use a N/10 potassium bromide and then, *after filtration*, to titrate with the starch iodide. Starch iodide reacts with the chloride, bromide, cyanide, or sulphocyanate of silver, so that these salts must

<sup>1</sup> Compare Mylius: Ber. d. chem. Ges., 20, 688. The statement made above is intended to apply only to iodide of starch prepared by the aid of *heat*, as described in the present paper.

always be filtered out before proceeding to the al titration.

### *Auxiliary Solutions.*

Iron solution C contained 40 grams ferrous am sulphate and 40 grams ferric ammonium sulphate v cc. dilute sulphuric acid to the liter. For reasons already given, it is desirable to have solutions of ferrous and ferric salts free from sulphates to use for this method. Experiments were accordingly made with solutions obtained from iron and dilute nitric acid, containing about 28 grams of iron to the liter and were successful. Such solutions have the disadvantage of gradually becoming deep brown in consequence of the formation of basic ferric nitrate, and they contain organic matter derived from the carbon of the iron. This organic matter takes up a little iodine and therefore decolorizes starch iodide. Solutions prepared from strontium nitrate with solutions of ferrous and ferric sulphates are free from the latter objection but not entirely from the former.

Instead of ferrous solutions, those of nitrous acid may be employed as previously mentioned. They may suitably be prepared by dissolving 30 grams of sodium nitrite (free from chloride) in one liter of dilute nitric acid (13 per cent). Such a solution is designated "Sol. D" in the following tables.

### *Experiments on the Influence of Dilution and Degree of Acidity.*

In the first series of experiments recorded below, a solution (slightly acid) of silver nitrate containing 0.7887 gram of silver was used and an empirical solution of starch iodide, of which 1 cc. = 1.639 mg. of silver designated as "sol B."



Series I.

Expt. No.	cc. Ag solution.	cc. H <sub>2</sub> O added.	cc. dilute HNO <sub>3</sub> added.	cc.	cc. nitrous acid or iron solution.	cc. iodide of starch required.	Remarks.
46	25	None	....	4	Sol. D.	13.90	End reaction sharp.
47	25	250	....	20	Sol. D.	13.25	" " "
48	25	None	1	2	Fe Sol. C.	11.85	Ag <sub>2</sub> SO <sub>4</sub> precipitated
49	25	"	5	2	"	11.85	" "
50	25	250	5	2	"	12.20	" "
51	25	250	5	2	"	12.17	" "
52	25	1000	5	2	"	12.65	" "
53	25	1000	20	2	"	12.67	" "
54	25	1000	20	8	"	12.63	" "
55	25	100	5	2	"	12.11	" "

Series II, 2 cc. of Iron Solution (C) Added in Each Experiment.

Expt. No.	cc. Ag solution.	cc. H <sub>2</sub> O added.	cc. dilute HNO <sub>3</sub> added.	cc.	cc. Pb or Cu solution.	cc. iodide of starch required.	Remarks.
56	25	250	5	10	N/10 Pb(NO <sub>3</sub> ) <sub>2</sub>	12.21	
57	25	250	5	10	"	12.18	
58	25	None	5	10	"	11.57	{ Ag <sub>2</sub> SO <sub>4</sub> precipitated with PbSO <sub>4</sub> .
59	25	25	5	10	"	11.97	{ Ag <sub>2</sub> SO <sub>4</sub> precipitated with PbSO <sub>4</sub> .
60	25	250	5	10	"	12.20	
61	25	None	5	10	"	12.02	{ Ferrous nitrate used instead of sulphate.
62	25	"	5	10	" (v. No. 58)	11.65	
63	25	250	5	10	N/10 Cu(NO <sub>3</sub> ) <sub>2</sub>	12.20	
64	25	None	5	10	"	11.88	{ Ag <sub>2</sub> SO <sub>4</sub> precipitated.

Series III, Iodide "Sol. A" (See page 261), adjusted to =  $N/10$  Silver Solution. "B" is an Arbitrary Solution of Silver Nitrate.

Expt. No.	cc "Sol. B."	cc. H <sub>2</sub> O added.	cc. HNO <sub>3</sub> .		cc. iron solution.	cc. "Sol. A" required.	Remarks.
65	25	150	2	conct.	8 Fe sulphates	18.27	
66	25	150	12	"	8 "	18.30	
67	25	150	2	"	2 "	18.25	{ Very quick titration.
68	25	None	2	"	Fe(NO <sub>3</sub> ) <sub>3</sub> from Fe	18.18	{ Very slow titration.
69	25	"	2	"	FeSO <sub>4</sub> +Sr(NO <sub>3</sub> ) <sub>2</sub>	18.25	{ Very slow titration.
70	25	"	10	"	FeSO <sub>4</sub> +Sr(NO <sub>3</sub> ) <sub>2</sub>	18.25	{ 5 cc. satur'ed sol. NaNH <sub>4</sub> HPO <sub>4</sub> .
71	25	150	2	"	8 Fe sulphates	18.27	{ 25 cc. $N/10$ Pb(NO <sub>3</sub> ) <sub>2</sub> sol.
72	25	150	4	"	4 Fe nitrate sol.	18.25	
73	25	None	20	dil.	FeSO <sub>4</sub> + Sr(NO <sub>3</sub> ) <sub>2</sub>	18.21	
74	25	150	20	dil.	FeSO <sub>4</sub> + Sr(NO <sub>3</sub> ) <sub>2</sub>	18.27	
75	25	None	20	dil.	FeSO <sub>4</sub> + Sr(NO <sub>3</sub> ) <sub>2</sub>	18.21	
76	25	50	.....		12 cc. nitrous acid, "Sol. D"	18.15	
77	25	100	.....		10 cc. nitrous acid, "Sol. D"	18.22	
78	25	100	.....		10 cc. nitrous acid, "Sol. D"	18.25	
79	25	100	.....		5 cc. nitrous acid, "Sol. D"	18.23	
80	50	None	.....		10 cc. nitrous acid, "Sol. D"	36.36	

From these results the following conclusions may be drawn :

I. Within certain limits the amount of free nitric acid is without appreciable influence.

II. A considerable excess of iron solution is without influence.

III. For increasing dilution a very small correction is called for which amounts to 0.10 mg. of silver for each 100 cc. of solution. This correction is to be subtracted from the results directly obtained.

IV. If the solution titrated contains much more than 20 mg. of silver per 100 cc. the results are too low in consequence of precipitation of silver sulphate with the iodide. This influence also appears in experiments numbered 58, 59, 62.

The object of the second series, experiments 56 to 62 inclusive, was to show the influence of lead salts upon the titration. It is apparent that there is no influence except when in consequence of insufficient dilution the precipitate of lead sulphate carries down silver sulphate with it as is shown in numbers 58 and 62, and to a less extent in number 59, where the addition of 25 cc. of water renders the results almost normal. That these errors are really due to the sulphate and not to the lead is shown by number 61 in which the same amount of lead salt was used but no sulphate, ferrous and ferric nitrate solution being substituted for it. The titrations in the presence of copper nitrate, numbers 63, 64, show that this salt, as might be expected, is without influence on the result. The solution of lead contained 20.7 grams of the metal per liter; that of copper 63.3 grams. There was accordingly about five times as much lead present as silver or about one and a half times as much copper.

Under Series III a number of observations have been brought together upon the titration of larger amounts of silver, in more concentrated solution and under varying conditions, with the combined solution of starch, potassium iodide and iodine. The deductions to be drawn from these data, in addition to those already derived in the foregoing pages may be enumerated as follows :

I. The correction for dilution does not exceed 0.02 cc. of the N/10 solution for each 100 cc. additional water.

II. The influence of varying speed of titration is inappreciable.

III. The influence of varying amounts of free acid (above a certain minimum) or of ferrous salt, is inappreciable.

IV. The results obtained by the use of nitrous acid as a deoxidizer are not directly comparable with those obtained when the ferrous and ferric salts are used, being lower when the solution is concentrated and higher (see Experiments 46 and 47) when dilute.

The results with the iron salts are also more constant and the reaction quicker.

V. Phosphates and lead salts are without influence.

Other experiments, not necessary to detail, show that arsenates and antimonates are without influence.

On the basis thus secured it is possible to lay down a general

*Method of Procedure.*

The silver solution to be titrated should be acid with nitric acid but ought not to contain enough of this reagent to oxidize a ferrous salt in the cold; that is, it should contain less than five per cent of the acid,  $\text{HNO}_3$ . It must be free from mercury and from the lower oxides of arsenic and antimony, but may contain sulphurous acid.

Add a ferrous salt in such amount that at least as much iron shall be present as silver and an equal quantity of a ferric salt. An excess of the latter must be added if the original solution contained sulphurous acid. If nitrous acid is present it must first be removed by boiling.

The mixture of ferrous and ferric salts are best kept on hand in the form of sulphates which, just before use, are converted into nitrates by the addition of a moderate excess of strontium or lead nitrate solution, the last step being superfluous when the silver solution contains less than 20 mg. silver per 100 cc.

The titration is to be carried on with constant stirring and not too rapidly. Under these conditions the end reaction is never in doubt to the extent of even 0.05 cc., provided that all reagents used are perfectly free from chlorine. A subsequent bleaching of the solution in the course of an hour or two is to be disregarded. A porcelain dish is much more suitable than a beaker for the titration on account of the uniform, white background.

*Applications.*

The method described is obviously applicable in many ways to residual analyses, as of chlorides, cyanides, etc., and appears especially suitable to the determination of small quantities of these substances as in water analysis. The author intends to elaborate the process further, and desires to reserve the field for a reasonable time.

## THE ESTIMATION OF FAT IN SWEETENED CONDENSED MILK BY THE BABCOCK TEST.

BY E. H. FARRINGTON.

The Babcock test is now a standard method for the estimation of butter-fat in nearly all kinds of dairy products. It is universally used for examining whole milk, skim-milk, buttermilk, whey, and cream, and it has also been successfully applied to the determination of fat in cheese and in condensed milk containing no sugar. A large proportion of the canned condensed milk, however, is sweetened with cane-sugar, and up to the present time no satisfactory way of testing this sweetened milk has been devised. Instead of the clear fat, a black, flocculent substance separates in the neck of the test-bottles, and when carried out in the usual way it is impossible to obtain a satisfactory reading with such milk.

Many attempts have been made to obtain a clear separation of fat by using more or less acid, or acid of different strengths, but these modifications have not overcome the difficulties. The common way of determining fat by extracting the sweetened condensed milk with ether is also unreliable, so that chemists have not had any satisfactory method for estimating the fat in condensed milk to which sugar has been added.

Since it is evident that the excess of cane-sugar is responsible for this poor separation of the fat, some way of removing this sugar must be devised in order to make any method of analysis successful. This I have found can be done by a few changes in the ordinary manipulation of the Babcock test.

In order to wash out the sugar without removing any of the fat in the washings, I first had a test-bottle made with two necks. One of these is the usual graduated neck, and the other is a side tube of about the same bore and fully as long as the neck tube, but extending to the inside bottom of the test-bottle. By means of this side tube the sugar solution can be siphoned out of the test-bottle after the curd has been separated with a few drops of acid.

A number of trials with this test-bottle showed that the excess of sugar could be removed in this way and that a clear

separation of the fat is afterwards obtained by completing the test in the usual manner. It soon became evident, however, that the side-tube was superfluous, and that the whey could be poured off from the curd through the graduated neck of the test-bottle as safely as it was siphoned through the side tube. This is made possible by whirling the test-bottles in a steam-heated centrifuge at such a speed that the curd is cooked into a rather hard lump, which does not break when the whey is poured off.

A brief description of the manipulation adopted will explain the method that has proved satisfactory.

From 40-60 grams of condensed milk are weighed into a 200 cc. graduated flask; about 100 cc. of water are added, and the solution of the condensed milk effected. The flask is then filled to the mark with water, and, after mixing thoroughly, a 17.6 cc. pipette full is measured into a Babcock test-bottle. About 3 cc. of the sulphuric acid commonly used for testing milk are added, and the milk and acid mixed by shaking the bottle vigorously. The milk is curdled by the acid, and the curd and whey separated somewhat. In order to make this separation complete and to compact the curd into a firm lump, the test-bottle is whirled for about six minutes at rather a high speed (1,000 rev.) in a steam-heated turbine centrifuge.

The chamber in which the bottles are whirled ought to be heated to about 200° F. This can be done either by the turbine exhaust steam which leaks into the test-bottle chamber of some machines, or by means of a valve and pipe which will allow steam to be turned directly into the test-bottle chamber. After this first whirling, the test-bottles are taken from the centrifuge, and by being careful not to break the lump of curd, nearly all the whey or sugar solution can be poured out of the neck. Ten cc. of water are then poured into the test-bottle, and the curd is shaken up with it so as to wash out more of the sugar. Three cc. of acid are then added as before and the test-bottle whirled a second time in the centrifuge. The whey is decanted again, and this second washing removes so much of the sugar that it will not interfere with testing in the usual way. The curd remaining in the test-bottle after the second washing is shaken up with 10 cc. of

water, and to this water-emulsion of the curd the usual amount, 17.5 cc., of sulphuric acid is added and the test completed in the same way as milk is tested. The amount of fat finally obtained in the neck of the test-bottle is calculated to the weight of condensed milk taken.

Several analyses of the same sample were made using a different weight of condensed milk each time. The results, when calculated to the original substance, gave as nearly the same percentage of fat as could be expected from duplicate analyses.

Five brands of sweetened condensed milk were examined by this process, at least four determinations being made of each sample. The fat separated was clear and the final results satisfactory.

Sixty grams of the condensed milk is about the right amount to take in a 200 cc. flask, then each 17.6 cc. pipette full of this 200 cc. is equal to 5.28 grams of the sample tested. The common brands of condensed milk will give a reading from this weight of about 2 per cent on the neck of a Babcock test-bottle. The volume of fat occupied by 1 per cent on the scale of the test-bottle is equal to 0.18 gram fat, and 3 per cent would show 0.54 gram fat, which is 10.22+ per cent of the 5.28 grams condensed milk tested.

The following results were obtained with the five samples examined, each sample was tested four or more times, with a very satisfactory agreement of results in each case :

Sample No.	Weight and dilution of condensed milk tested.	Test-bottle reading.	Per cent fat in condensed milk.
1	60 grams to 200 cc.	2.4	8.00
1	29.6 " " " "	1.25	8.00
2	32.7 " " " "	1.6	10.00
3	51.6 " " " "	2.4	9.30
4	45.4 " " " "	2.3	10.35
5	65.8 " " " "	2.0	6.35

The condensed milk may be transferred to the weighed measuring flask by means of a glass funnel which reaches to the bulb of the flask, pouring the thick liquid previously mixed with a spatula directly from the tin can into the funnel through which it will run freely if the throat of the funnel is large enough.

Careful tests of the whey poured off from the test-bottles showed that no fat was lost by this decantation if the whey was clear and contained no pieces of curd.

It is essential that the curd should be cooked in the test-bottle so as to cause it to shrink into a compact lump, which does not break when the whey is poured off.

If only 20 grams condensed milk are measured into a 200 cc. flask, a difference of 0.2 per cent of fat on the neck of the test-bottle amounts to about 2 per cent fat in the original substance. It is therefore well to test a more concentrated solution of the milk than this. As stated above, about 60 grams to 200 cc. give a satisfactory solution.

DAIRY SCHOOL,  
UNIVERSITY OF WISCONSIN, MADISON, WIS.,  
July 24, 1900.

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Contribution from the North Carolina Agricultural Experiment Station.

## THE PURIFICATION OF PHLOROGLUCINOL.

BY G. S. FRAPS.

In the determination of pentosans in vegetable materials, the substance is distilled with hydrochloric acid of 1.06 sp. gr., the furfural precipitated with phloroglucinol, and the precipitate weighed.

Commercial phloroglucinol contains diresorcinol as an impurity, which is difficultly soluble in hydrochloric acid of 1.06 sp. gr. According to Kruger and Tolleus,<sup>1</sup> small quantities of diresorcinol do not affect the determination; but Counciler<sup>2</sup> found from 7.5 to 14.6 per cent of diresorcinol in commercial pure phloroglucinol, and concludes that it varies greatly in composition, and often contains enough diresorcinol to vitiate the results. The methods of analysis of the Association of Official Agricultural Chemists of this country, require the use of a phloroglucinol free from diresorcinol for the determination of pentosans. The bar to the use of this preparation is its great price, as it costs nearly its weight in gold.

Since the diresorcinol is difficultly soluble in hydrochloric acid of 1.06 sp. gr., and 100 cc. of the acid dissolves 0.7 gram phloroglucinol at 15° C., phloroglucinol can be purified

<sup>1</sup> Ztschr. angew. Chem., 1896, 40.

<sup>2</sup> Chem. Zeit., 1897, 2.



by dissolving it in hydrochloric acid, and allowing the diresorcinol to crystallize out. The diresorcinol which remains in solution will not affect the accuracy of the determination.

The method of purification is as follows: About 300 cc. of hydrochloric acid, 1.06 sp. gr., are heated in a beaker and 11 grams commercial phloroglucinol added in small quantities at a time, stirring constantly until it has almost entirely dissolved. Some impurities may resist solution, but it is unnecessary to dissolve them. The hot solution is poured into a sufficient quantity of the same hydrochloric acid (cold) to make the volume 1500 cc. It is allowed to stand at least over night—better several days—to allow the diresorcinol to crystallize out, and filtered immediately before using. The solution may turn yellow, but this does not interfere with its usefulness. In using it, the volume containing the required amount is added to the distillate from the pentosan.

The phloroglucinol solution prepared in this manner has been compared with phloroglucinol free from diresorcinol, and found to give as good results. Duplicate analyses of substances containing pentosans agreed as well as could be expected. On three solutions of furfural, the weights of precipitates were, using phloroglucinol:

	I.	II.	III.
	Gram.	Gram.	Gram.
Purified as above described	0.4575	0.5115	0.4647
Merck's, free from diresorcinol	0.4620	0.5124	0.4671

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## THE WIDE OCCURRENCE OF INDICATORS IN NATURE.

BY G. S. FRAPS.

In the course of some work on a black cow-pea bean, the writer's attention was attracted by the change from black to red, which took place when it came in contact with an acid. Later, in speaking to Mr. G. H. Whiting, a student, about this, he mentioned that the juice of the blackberry had the properties of an indicator. These observations led to the work about to be described. Since completing it, the writer has been informed that a lady placed some violets in ammo-

nia water to preserve them, and to her astonishment, they became green.

The results of this work show that indicators are of very common occurrence in nature. Some seventy-four kinds of colored flowers, both wild and cultivated, the leaves of five varieties of coleus, the cow-pea bean, the blackberry, mulberry, smilaxberry, strawberry, and the red beet were extracted with water or dilute alcohol, and the extract tested for indicators. In only three cases did the extract not become one color when acid and another color when alkaline. As a rule, the coloring-matter was fairly sensitive as an indicator, being changed by from less than 1 to 2 drops of tenth-normal ammonia. Some of the changes were very sharp, and many of the colors were very beautiful. In some cases the color passed through several stages in going from acid to alkaline, or the reverse.

The materials examined could be grouped in four classes :

*Class I.*—Extract not affected by acid or alkali.

*Class II.*—Extract colorless when acid, yellow when alkaline.

The flowers in this class were yellow, and the yellow coloring-matter was hardly affected by the extracting agent.

*Class III.*—Extract red (or a shade of red) when acid, yellow when alkaline.

*Class IV.*—Extract red when acid, green when alkaline.

Classes III and IV are not sharply separated, sometimes the color produced by the alkali being such that it was hard to decide whether it was yellow-green or green-yellow. Ammonia was the alkali used ; often a green solution with ammonia would have been yellow with caustic soda. Most of the coloring-matters in these two classes were very sensitive. In many cases the flowers were bleached when boiled with water, and the extract nearly colorless, or quite so, but it would become colored when made acid or alkaline.

*Class V.*—Miscellaneous. This includes all that do not fall in the other four classes. It must be observed that in no case do the colors occur in the reverse order from those in the other classes—that is, never colorless when alkaline and yellow acid, or red when alkaline and green or yellow acid.

The colors of the coleus especially, depend on the degree of acidity of the leaf as well as on the kinds and distribution of the colors. With coleus colors there is a regular change in color from acid to alkaline, or the reverse, passing through several stages. It is easy to see that a slight change in the acidity of the sap of the leaf will affect the color and give rise to some of the manifold variations that are observed in the coleus. The same may be said of some flowers.

#### *Methods of Examination.*

Two methods were adopted for testing the color. In the one, small portions of the material were placed into two test-tubes with alcohol, a few drops of fifth-normal hydrochloric acid added to one, of tenth-normal caustic soda to the other, and the changes noted. It usually requires some time for the effect to be visible. In the second method the material was boiled in a large test-tube with about 20 cc. of water, to which a little alcohol was often added, cooled, the extract poured off, and titrated with fifth-normal acid and tenth-normal ammonia. The two methods usually gave the same results, though they were sometimes different, as was to be expected, as in the one case all of the color, soluble and insoluble, was subjected to the action of caustic soda; in the other case only the soluble part was treated with ammonia. Method 2 allowed some conclusion as to the sensitiveness of the color to be made :

*Class I.*—Color unaffected by acid or alkali. This includes the orange flowers of *Stylosanthus biflora*, the yellow ones of *Chrysogonum Virginianum*, and the leaves of a smooth, red variety of coleus. Three materials not containing indicators were found out of 81 examined.

*Class II.*—The flowers in this class give a colorless extract which becomes yellow when made alkaline.

The color is moderately sensitive. All of the flowers but one—the white petals of the wild daisy—are yellow or orange. Yellow is a color which cannot be extracted by boiling water. In some cases it goes into solution with the tenth-normal caustic soda.

This class comprises 10 ; stamens of begonia and *Solonum*

*Carolinaense*; petals of canna, *Oenothera sinuata*, *Hypoxis erecta*, butter-cups, alamander, wild daisy, a yellow wild flower, and leaves of the yellow coleus.

*Class III.*—In this class the materials give an extract which are red or a shade of red when acid, yellow or a shade of yellow when alkaline. All the colors are fairly sensitive, being changed by at least two drops of tenth-normal ammonia. Twenty-one of the 81 materials examined fall into this group, 11 being originally red or pink flowers, 4 orange or yellow, 5 purple or violet, 1 green (coleus leaf). The red and pink flowers were: the pink, rose (faint pink, rose, and wild rose), pink larkspur, crimson clover, phlox (faint pink, light claret, rose, scarlet, magenta), begonia (2 varieties), double oleander, a variety of *Eupharbia*, *Spensonia goliagefolia* rosa, *Clerodendrum*, and *Silene Virginica*. With the exception of *Clerodendrum*, which gave a well-colored, orange-pink solution, all of the flowers above named were bleached when boiled with water, giving a colorless or faintly colored solution, which, however, became colored on the addition of acid or ammonia. Verbena flowers gave extracts, yellow with caustic soda, but green with ammonia, and the extract from sweet peas green when first made alkaline, became yellow on standing. These two are included in Class IV.

The purple or violet flowers were, the vetch, Mexican sage, heliotrope, *Clematis ochroleuca*, and *Solomon Carolinaensis*. They were bleached by the boiling. The orange or yellow flowers were orange nasturtium and canna, *Asclepias tuberosa*, yellow *Alamander vereofolia*. The yellow color of the flower was unaffected, but a colorless or faintly colored extract was formed which became colored on addition of acid or ammonia. A red-orange extract was obtained from the green part of the leaf of a red and green coleus, which was red with acid and brown-yellow with ammonia.

*Class IV.*—This includes those coloring-matters which are a shade of red when acid, a shade of green when alkaline. The greens are at times of a beautiful emerald color, sometimes of a yellowish tinge. Most of the colors are very sensitive to the reagents, being affected by less than 1 drop of tenth-normal ammonia.

Thirty of the materials examined fall into this class, 15 being originally a shade of red, 9 violet or purple, 3 blue, 1 lilac, 1 black (bean), 1 yellow. The flowers a shade of red were: red clover, scarlet sage, Canterbury bell, red zinna, rose geranium, crimson honeysuckle, California poppy, verbenas (faint pink and rose), sweet peas (faint pink, rose, maroon, magenta, lavender), gladiolus (rose), red cyclomen, varieties of *Bumaldae*, hibiscus, *Tephrosia* (devil's shoestring), and leaves from four varieties of coleus. With the exception of hibiscus, scarlet sage, and coleus, the extracts from these were colorless or nearly so.

The purple or violet flowers were phlox, petunia, coriopsis, verbenas, sweet peas, "Jimson weed," maypop, or passion flower, *Specularia perfoliata* and *Ruellia ciliata*.

The lilac flower was *Salvia urtica*, the blue ones were *Ageratum*, *Runella vulgaris*, and blue larkspur, the yellow one was nasturtium, and the black material, a cow-pea bean.

The colors from some of these flowers passed through several stages on the way from acidity to alkalinity. The most noteworthy are:

*Specularia perfoliata*: Magenta, blue, green.

*Ruellia ciliata*: Rose, lilac, green.

*Salvia urtica*: Claret, peacock blue, green.

"Jimson weed": Magenta, purple, green.

Maypop: Magenta, blue, green-blue, olive green.

Blue larkspur: Magenta, purple, blue, peacock-blue, green.

Purple petunia: Magenta, purple, blue, green.

California poppy: Magenta, purple, violet, peacock-blue, green.

Red coleus: Red, claret, violet, green.

Red and yellow coleus: Rose, brown-red, orange-red, yellow-green, olive-green.

Light red, dark red, and green coleus: Cherry, violet, brown, green-brown, dirty green.

Red and deep red coleus: Magenta, purple, blue, green.

Most of the colors above given were very bright and beautiful, and, as a rule, fairly sensitive.

The coloring-matters of the following flowers in this group

are especially sensitive: "Jimson weed," Maypop, *Salvia urtica*, black cow-pea (bean), *Ruellia ciliata*.

*Class V.*—This group includes substances giving colors with acid and alkali that do not come into the classes already described.

The colors are those produced by ammonia. The color, when acid, is given first, then the stages it passes through to alkaline:

*Bougainvillea spectabilis* (mauve): Purple, colorless.

*Gloxinia hybridia* (pink): Pink, purple, brownish red.

" " (purple): Magenta, purple, olive-green.

*Dendrobium nobilia* (purple): Pink, purple, blue, green.

*Amaryllis* (red): Cherry, maroon.

*Salvia* (red): Orange, dark red.

*Cynthia* (yellow): Yellow, terra-cotta.

Geranium (scarlet): Scarlet, violet.

*Galardium* (red): Scarlet, corn, yellow-brown.

Snapdragon (red): Red, red-brown.

Canna (red): Red, orange-brown:

Fruit:

Smilaxberries (red): Pink, violet.

Beets (red): Magenta, purple.

Strawberries: Straw, purple.

Blackberries: Rose, colorless.

Mulberries: Cherry, violet.

Brown cow-pea bean: Colorless, brown.

LABORATORY OF THE N. C. COLLEGE  
OF A. and M. ARTS, June, 1900.

## A NEW SYNTHESIS OF SECONDARY AMINES.

BY ALFRED TINGLE.

### *Theoretical.*

It has been already shown<sup>1</sup> that when methylic salicylate is boiled with aniline the chief products are methylaniline and phenol. In the present research an attempt has been made to extend this reaction to the production of other diamines. A study has been made of the action of ethylic and isoamyllic

<sup>1</sup> This JOURNAL, 24, 57.

see entry V. 25 p. 172

salicylates on aniline and of methylic salicylate on ammonia.

When ethylic salicylate and aniline are boiled together for seven hours the reaction between them is extremely slight, and most of the ester can be recovered unchanged. A small quantity of salicylanilide is formed, with a varying amount of phenol, and a base, the hydrochloride of which melts at  $172^{\circ}$ – $174^{\circ}$ . The quantity of the latter obtained was too small for purification and analysis, even when 16 grams of ester were used in its preparation, but its melting-point is in agreement with that given by Reynolds<sup>1</sup> for ethylaniline hydrochloride.

Under like circumstances, isoamylic salicylate and aniline react to about the same extent. In this case no salicylanilide appears to be formed at all; 20 grams of isoamylic salicylate gave only 0.3 gram of phenol; the hydrochloride of a base, probably isoamylaniline, was obtained, but not in quantity sufficient for analysis. It melted at  $181^{\circ}$ – $182^{\circ}$ , was very soluble in water, and did not form a stable chloroplatinate. This latter fact is in accordance with the statement of A. W. Hofmann,<sup>2</sup> who first described isoamylaniline and its hydrochloride. Unfortunately, neither he nor Spady,<sup>3</sup> who subsequently obtained them, have left any record of the melting-point of the latter. Limpricht<sup>4</sup> has shown that alcoholic ammonia reacts with methylic salicylate, giving salicylamide. In the present research, gaseous ammonia was passed into boiling methylic salicylate, and the gaseous reaction-products were absorbed in water. Under these circumstances dimethylamine is formed. Its chlorplatinat has been prepared and analyzed. Its formation does not seem to be accompanied by that of any mono- or trimethylamine.

The large amount of unchanged ammonia which accompanies the amine constitutes the chief difficulty which has to be overcome in its preparation by this method. The reaction between methylic salicylate and ammonia gas is not so simple as that between alkylsalicylates and aniline. The products formed simultaneously with dimethylamine, and which remain dissolved in the unchanged methylic salicylate, have not yet been fully

<sup>1</sup> J. Chem. Soc. (London), 1892, 455.

<sup>2</sup> Ann. Chem. (Liebig), 74, 153.

<sup>3</sup> Ber. d. chem. Ges., 18, 3377.

<sup>4</sup> Ann. Chem. (Liebig), 98, 258.

investigated, but it would appear that phenol is not among them.

The present investigation, as far as it has been carried, shows, therefore, that alkyl salicylates are capable of introducing their alkyl group into the aniline molecule, forming monalkylated anilines. This reaction takes place with difficulty when the alkyl group is other than methyl. Methyl salicylate is also capable of introducing two methyl groups into ammonia, forming dimethylamine. The formation of primary or tertiary amines by this reaction has not been observed, and it is believed that its chief practical value, if it should prove to possess any, will depend on this circumstance.

It appears that the only means previously recorded for the preparation of isoamylic salicylate is that of Drion,<sup>1</sup> which depends on the interaction of salicyl chloride and amylic alcohol. The writer obtained an excellent yield of ester by using an extension of Fischer's method, boiling together amylic alcohol, salicylic acid, and a small quantity of concentrated sulphuric acid.

#### *Practical.*

*Preparation of Isoamylic Salicylate.*—To obtain the isoamylic salicylate employed in these experiments, an extension of Fischer's esterification method was used: 50 grams of salicylic acid, 100 cc. of commercial amylic alcohol, and 15 cc. of concentrated sulphuric acid were boiled together for three hours. When cold, the product was washed with a solution of sodium carbonate and extracted with ether. The ethereal layer, after being dried over calcium chloride, was submitted to a single fractional distillation. The fraction passing over between 265° and 275° was accepted as isoamylic salicylate, the boiling-point of which is stated by Drion<sup>2</sup> to be 270°. The yield of ester so obtained was 59.6 grams. From the alkaline washings 6.6 grams of salicylic acid were recovered.

*Action of Ethylic Salicylate on Aniline.*—16.6 grams (1 mol.) of ethylic salicylate, and 27.9 grams (3 mols.) of aniline were boiled together in a Kjeldahl flask for more than seven hours.

<sup>1</sup> Compt. rend., 39, 122; Ann. Chem. (Liebig), 92, 313.

<sup>2</sup> Loc. cit.



The mixture was then transferred to a Würtz flask and distilled; the greater portion of the liquid passed over between  $185^{\circ}$  and  $215^{\circ}$ . The small tarry residue was crystallized from dilute alcohol. It then melted at  $126^{\circ}$ , and was identified as salicylanilide.

The distillate was acidified with dilute hydrochloric acid and extracted with ether. The extract consisted almost entirely of unchanged ethylic salicylate, but in most experiments traces of phenol were also detected.

The free bases were subsequently obtained by the addition of alkali to their acid solution, and extraction with ether. Fractional distillation of the mixture gave a few drops of oil boiling above  $190^{\circ}$ . Its sulphate was readily soluble in water. Its hydrochloride was still more so, and melted at  $172^{\circ}$ – $174^{\circ}$ . The quantity obtained was entirely insufficient for analysis, but there can be little doubt that it is identical with ethylaniline hydrochloride, the melting-point of which is given by Reynolds<sup>1</sup> as  $172^{\circ}$ – $173^{\circ}$ .

*Action of Isoamylic Salicylate on Aniline.*—20.9 grams (1 mol.) of isoamylic salicylate and 27.9 grams (3 mols.) of aniline were boiled together in a Kjeldahl flask for six hours. On distilling the mixture two fractions were obtained boiling respectively above and below  $200^{\circ}$ . No salicylanilide could be detected in the tarry residue. The more volatile portion of the distillate was shaken with a solution of potassium hydroxide and the excess of aniline extracted with ether. On subsequently acidifying the alkaline liquid 0.3 gram of phenol was obtained. This was identified by its smell, and by the formation of tribromphenol.

The less volatile fraction resulting from the above distillation was treated with dilute sulphuric acid, and unchanged isoamylic salicylate was extracted with ether. The bases present were obtained by neutralization of the acid solution and extraction with ether. They were afterwards dissolved in aqueous hydrochloric acid. On evaporating this solution, crystals separated, melting at  $194^{\circ}$ – $195^{\circ}$ . These were identified as aniline hydrochloride (m. p.  $195^{\circ}$ ). The mother-liquor from the crystals, on further evaporation, gave a crop of much

<sup>1</sup> *Loc. cit.*

smaller crystals, melting definitely at  $181^{\circ}$ – $182^{\circ}$ . It seems probable, considering the manner of their formation, that these are isoamylaniline hydrochloride. No record appears to have been made of the melting-point of this substance, which has been described by A. W. Hofmann<sup>1</sup> and by J. Spady.<sup>2</sup> It was not found possible to prepare the chlorplatinate in a pure condition (which so far agrees with Hofmann's statements), and the quantity obtained was so small as to render analysis by any other method impossible.

*Action of Ammonia on Methylic Salicylate.*—Dry ammonia gas was conducted into a flask containing boiling methylic salicylate. The tube delivering the ammonia was made to dip far below the surface of the liquid. A second tube, high in the neck of the flask, allowed the gaseous products to escape, and led them into an absorption flask containing water. Provided that a long-necked flask was used, it was found that a condenser was not necessary to prevent the carrying over of ester. The action was allowed to proceed for thirty minutes in the first experiment, but in subsequent ones this was increased to three hours. At the end of this time the contents of the absorption flask were neutralized with hydrochloric acid, and the resulting solution was evaporated to dryness. The residue was extracted with boiling absolute alcohol, and the solution so obtained was evaporated in its turn, the resulting solid being freed from any remaining ammonium chloride by a second extraction. To this alcoholic solution platinic chloride was added; the yellowish precipitate which at once formed was filtered off, dried at  $100^{\circ}$ , and analyzed.

Two determinations, from separate preparations, were made :

I. 0.0326 gram of chlorplatinate gave 0.0139 gram of platinum on ignition, or 42.63 per cent.

II. 0.1073 gram of chlorplatinate gave 0.0464 gram of platinum on ignition, or 43.24 per cent.

Calculated for  $[\text{NH}_2(\text{CH}_3)_2]_2\text{PtCl}_6 = 42.99$  per cent Pt.

The yield of dimethylamine is small in proportion to the quantity of ammonia which passes over. The substances simultaneously formed and retained in solution by the excess of

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Loc. cit.*

methylic salicylate have not yet been thoroughly investigated. Among them a small quantity of salicylamide has been found and identified by the fact that it melted at  $137^{\circ}$ . No phenol has been detected. The writer proposes to continue and extend this research.

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## NOTE.

### *On Higher Superoxides of Hydrogen.*

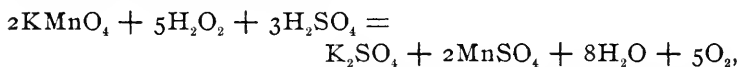
About three years ago A. Bach<sup>1</sup> noted that the oxidation-products of nascent hydrogen, produced from palladium hydride, oxidize indigo solutions more rapidly than hydrogen peroxide does. This observation led him to the conclusion that during the slow oxidation of hydrogen a higher peroxide of hydrogen is formed; namely, hydrogen tetroxide,  $H_2O_4$ , analogous to potassium tetroxide.

In a recent paper Bach<sup>2</sup> has endeavored to determine experimentally whether higher superoxides of hydrogen exist.

The formation of hydrogen trioxide,  $H_2O_3$ , had already been suspected by Berthelot.<sup>3</sup> He noticed that, when potassium permanganate is titrated with hydrogen peroxide at low temperatures, the permanganate is decolorized without the liberation of oxygen. He concluded that this is due to the formation of a compound,  $H_2O_3$ , which is stable only at low temperatures.

The apparatus used by Bach in his work<sup>4</sup> is described by him in detail. It consists essentially of a burette so connected with a gas measuring-tube, that the solution under investigation can be titrated with potassium permanganate at the same time that the oxygen liberated can be collected and measured.

The author's criterion for the presence of a higher superoxide of hydrogen, is the amount of oxygen liberated when the solution is titrated with potassium permanganate. In accordance with the equation,



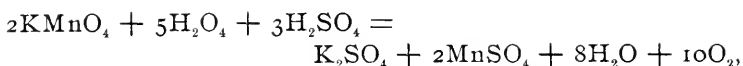
one molecule of oxygen is liberated for each molecule of hydrogen peroxide present, while, according to the equation,

<sup>1</sup> Compt. rend., 1897, 951.

<sup>2</sup> Ber. d. chem. Ges., 33, 1506.

<sup>3</sup> Ann. chim. phys., 1880, 146.

<sup>4</sup> Loc. cit.



each molecule of hydrogen tetroxide requires just as much potassium permanganate as a molecule of hydrogen peroxide, and twice as much oxygen is liberated.

In his experiments, Bach used the oxidation-products of hydrogen in the nascent state, hydrogen superoxide from potassium tetroxide, hydrogen superoxide from sodium dioxide and "Caro's acid." The last was prepared by treating a well cooled weak solution of hydrogen peroxide with concentrated sulphuric acid. If we represent by 1 the amount of oxygen liberated by hydrogen peroxide and potassium permanganate, then the amounts of oxygen liberated by corresponding amounts of the superoxides of hydrogen obtained from different sources are as follows :

Hydrogen peroxide.	Oxidation-products of hydrogen in the nascent state.	Hydrogen superoxide from sodium dioxide.	Hydrogen superoxide from potassium tetroxide.	"Caro's acid."
1	1.07	1.17	1.28	1.65

These results show that the solutions of the superoxides in question contained higher superoxides, which might be either hydrogen trioxide or hydrogen tetroxide. The author concludes from various considerations that hydrogen trioxide was not present.

From these experiments, then, it would seem that hydrogen tetroxide is capable of existence. The series of oxygen compounds of hydrogen hence consists of the following members :  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}_3$ ,  $\text{H}_2\text{O}_4$ . To this series should belong the suboxide  $\text{H}_4\text{O}$ . If Brühl's hypothesis of the tetravalence of oxygen is correct, this suboxide ought to be formed by the addition of hydrogen to water. Up to the present, however, all efforts to prepare it have failed. C. E. C.

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## CORRESPONDENCE.

### *To the Editor :*

The review of Arey's "Elementary Chemistry" which appeared in the April number of your Journal was written by one who so evidently fails to understand the book, or who holds opinions on the principles and methods of pedagogy which differ so widely from those of our best writers on the subject, that I desire that the other side of the case be submitted to your readers.

In his opening paragraph the reviewer states that the plan

of the book assumes that the pupil at the outset is capable of making good observations, an inference which is clearly illogical. The only assumption which a book intended to cultivate the observation makes, is that the first exercises in the book are adapted to the natural powers of the student. Continuing this topic the reviewer says, "This does not accord with experience." And here he makes a serious omission in that he fails to state whose experience he refers to. Most teachers have learned that children are keen observers, and that it is very easy to guide their observations by simple questions. It is only after the functional activity of this faculty has been atrophied by some so-called teacher who would reprimand a pupil for "venturing to express an opinion" as the reviewer says should be done, that the natural powers of observation fail to respond.

In the same paragraph the reviewer remarks, "It would certainly be interesting to read the note-books of pupils who without directions from the teacher should record the results of their first observations on chemical substances." In reply I beg to say that I think it would be interesting, and instructive also, to the reviewer.

I do not mean to say that it would be considered sound pedagogics to-day to give a beginner a complex organic substance and to require him to study it until he has learned all that is known about it; yet this was Agassiz' method, and where is there a greater teacher than he?

The modern teacher recognizes the soundness of Agassiz' method but saves time by arranging a course which, requiring at the outset only the most apparent observations and the most obvious inferences, gradually increases in difficulty of observation and in disciplinary value. He has found that the pupil's work and his thinking are best controlled by supplying directions for his experiments with questions which call for definite observations and inferences, including an occasional question which he cannot answer fully, to show him his limitations and to give him zest for further study.

The reviewer designates as "extremely dangerous" the experiment of exploding a mixture of potassium chlorate and sulphur and says that he shudders to think what the results would be if the experiment was performed by an inexperienced person. It is remarkable that after an honorable experience in the principal elementary chemistries of more than fifty years, this experiment should run amuck in this way. The writer has performed it regularly in his classes for twenty years, and having never had an accident, naturally wonders what manner of *pas de seul* the reviewer would execute if he should some-

time contemplate the results of the more dangerous experiment in which phosphorus is substituted for the sulphur of the above experiment; and yet the reviewer and other persons, often inexperienced, perform the latter experiment every time they strike a parlor match.

Now I am willing to admit that if large quantities of sulphur and potassium chlorate should be used, and if the experimenter chanced to secure a sufficiently intimate mixture of the two substances before any of it was exploded, the results might be serious, but the experiment is to be performed by the instructor, and from a personal acquaintance with the majority of the instructors of chemistry in New York State I can assure him that not one of them needs caution to use small quantities in such an experiment. However, fearing that perhaps the book might possibly fall into the hands of teachers who do need such caution, the author inserted a scare line in the teacher's handbook which accompanies the "Elementary Chemistry."

The next boomerang hurled by the reviewer has the following form: "On page 5 are found directions for an experiment which is not clear, though it sounds learned. The pupil is directed to weigh a quantity of sulphuric acid and a solution of calcium chlorid; then pour them together and weigh them again. The pupil is then asked: 'Does chemical action change the total quantity of matter in existence? Was the total quantity of sulphuric acid in the world increased or diminished by the above experiment? How was the total quantity of calcium chlorid affected?' As a matter of fact, the total quantity of sulphuric acid in the world is diminished by such an experiment, but the pupil cannot possibly know this unless told."(!)

This experiment is preceded by several experiments illustrating chemical change, in the last of which the student proves that in a given chemical change the factors have disappeared and an entirely distinct substance has been formed; with this in view they are fully able to answer the question which the reviewer says they could not possibly answer; in fact, in my last class, 31 of the 32 pupils did answer it without assistance.

The rest of the review consists of inferences concerning the personality of the writer, which are as uncalled for as they are unwarranted. To sum up: The reviewer writes from the standpoint of one who believes that the object of teaching chemistry is to make chemists of the pupils, whereas the book under review treats chemistry as a disciplinary subject.

ALBERT L. AREY.

# AMERICAN CHEMICAL JOURNAL

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Contributions from the Chemical Laboratory of the Rose Polytechnic Institute.

## XVIII.—CAMPHORIC ACID.

[NINTH PAPER.]

### STRUCTURE AND CONFIGURATION OF CISTRANSCAMPHOLYTIC ACID.

BY WILLIAM A. NOYES AND EDWARD F. PHILLIPS.

The opinion has been expressed by one of us<sup>1</sup> that cistranscampholytic acid and ciscampholytic acid (isolaunonic acid) are stereoisomeric bodies having the same structural formula. Walker<sup>2</sup> has recently expressed the same opinion as to the relation between the two acids, and has shown that each may be transformed into the other by means which seem to preclude any other explanation than that of stereoisomerism.

While we still hold the same opinion as to the structure of these acids, we have found that in one important point Walker and Cormack<sup>3</sup> have been led to a wrong conclusion. The cistranscampholytic acid obtained by the decomposition of dihydroaminocampholytic acid with nitrous acid<sup>4</sup> is optically ac-

<sup>1</sup> This JOURNAL, 17, 423; 23, 134; Ber. d. chem. Ges., 28, 551; 33, 57.

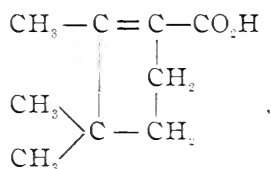
<sup>2</sup> J. Chem. Soc., 77, 383.

<sup>3</sup> Loc. cit., p. 377.

<sup>4</sup> This JOURNAL, 17, 424.

tive,  $[\alpha]_D = -59^\circ.6$  at  $18^\circ$ . The method of electrolysis used by Walker and Cormack evidently gives a small amount of the same acid, as they obtained the value  $[\alpha]_D = -5^\circ$  with the acid at first prepared. The acid which they obtained indirectly from ciscampholytic acid<sup>1</sup> is, probably, a racemic mixture of the right and left forms of the acid.

In his discussion of the optical properties of cistranscampholytic acid Walker assumes that an acid having the structural formula,



must necessarily be inactive because there is no single asymmetric carbon atom in the compound. For the ciscampholytic acid (isolaunonic acid) this conclusion is correct, since in that acid the methyl and carboxyl groups lie in the plane of the ring and that plane becomes one of perfect symmetry, the right and left sides being exactly alike. For such a body two optically opposite forms are impossible. This conclusion is in entire agreement with the results obtained by Blanc,<sup>2</sup> who has shown that ciscampholytic acid cannot be separated into two optically active forms. For the benefit of those who still hold to Bredt's formula for camphor it may be worth while to remark that the formula for ciscampholytic acid given above is the only one thus far proposed which does not imply that the acid is racemic instead of inherently inactive.

If we assign to dihydroaminocampholytic acid the configuration,<sup>3</sup>

<sup>1</sup> *Loc. cit.*, p. 580.

<sup>2</sup> *Bull. Soc. Chim.*, **21**, 832.

<sup>3</sup> This formula is based on the configuration for camphoric acid proposed some years ago by Aschan, which represents it as a "cis" compound. See Aschan: *Ber. d. chem. Ges.*, **27**, 2002; Noyes: *This JOURNAL*, **17**, 424; *Ber. d. chem. Ges.*, **28**, 551. Walker (*J. Chem. Soc.*, **77**, 395) has recently expressed the same view of the configuration of the acid, but appears to have overlooked the older statements.







there would not seem to be room for one of these groups within the ring; partly because, in accordance with Baeyer's theory of tension within polymethylene rings, another position for the atoms is found which implies far less tension than that just considered. This other position is indicated, somewhat imperfectly, by the manner in which formula II is written. By this method of writing it is intended to indicate that the doubly united carbon atoms no longer lie exactly in the plane of the other three atoms of the ring, but are thrown slightly out of that plane, the one on one side, the other on the other. The carboxyl and methyl groups connected with the same atoms will, in such a case, lie on opposite sides of the ring. A compound of this configuration has no plane of symmetry and may exist in a right-handed and a left-handed form.

So far as we are aware, no previous case is known in which an optically active body is formed by the addition of a halogen acid to an unsaturated compound, in which the only asymmetric carbon atoms present are those which become asymmetric through the addition of the halogen acid. In all other cases which have been studied the halogen may add itself equally on both sides of the double union and racemic mixtures are formed. An examination of the formula proposed for cistranscampholytic acid suggests a simple explanation for its remarkable conduct. In that formula the double union is accessible to the hydrobromic acid only on the outside, the other side of the double union being directed toward the inside of the ring and protected from the approach of the hydrogen and bromine; but the addition of the hydrobromic acid on the outside produces the configuration which corresponds to that of the hydroxy acid and of the original camphoric acid.

While the explanation given for the optical activity of the cistranscampholytic acid appears to be a logical development of current theories of stereomeric structure, the compound is at present the only one known<sup>1</sup> of an optically active body

<sup>1</sup> Some years ago Baeyer (Ber. d. chem. Ges., 27, 455) suggested that the activity of limonene might be due to a double union in a cyclic compound but another structure has now been assigned to the body. For other cases, in which optical activity has been erroneously ascribed to unsaturated compounds, see Bischoff and Walden, "Stereochemie", p. 841.

containing no asymmetric carbon atom in the ordinary sense.<sup>1</sup> The case is so peculiar and important from the theoretical standpoint, that it will be made, if possible, the subject of a more careful and extended study.

#### EXPERIMENTAL PART.

*Dihydroaminocampholytic Acid*,  $C_8H_{14} \begin{matrix} \swarrow NH_2 \\ \searrow CO_2H \end{matrix}$ .—This was prepared by the methods previously described.<sup>2</sup> Two determinations of the solubility gave 7.4 and 7.8 parts dissolved by 100 parts of water at 20°.

The saturated solution gave :

$$[\alpha]_D = +53^\circ.7.$$

*Dihydrohydroxycampholytic Acid*,  $C_8H_{14} \begin{matrix} \swarrow OH \\ \searrow CO_2H \end{matrix}$ .—The dihydroaminocampholytic acid was decomposed by treatment with dilute sulphuric acid and sodium nitrite,<sup>3</sup> the cistranscampholytic acid and the hydroxy acid were partly separated by ligroin, and the latter was crystallized from water or from acetic ether.

For the acid crystallized from water, 100 parts of water dissolved at 20°, 1.97 parts and for the saturated aqueous solution,

$$[\alpha]_D = +72^\circ.05.$$

For the acid crystallized from acetic ether, 100 parts of water dissolved 2.14 parts at 20° and gave :

$$[\alpha]_D = +71^\circ.55.$$

*Cistranscampholytic Acid*,  $C_8H_{13}CO_2H$ .—The acid which was obtained by extraction with ligroin was distilled with steam, the cistranscampholytic acid which passed over was taken up with ligroin and, after distilling most of the ligroin on the water-bath, the remainder was removed and the acid was dried by heating it on the water-bath, while the bulb containing it was evacuated.

<sup>1</sup> In one sense two asymmetric carbon atoms are present, since the two sides of the double union are unlike.

<sup>2</sup> This JOURNAL, 16, 503.

<sup>3</sup> *Ibid.*, 17, 424.

The acid obtained in this manner gave the following values for specific gravity and for specific rotatory power :

Temperature.	Specific gravity.	$[\alpha]_D$ .
13°.2	1.0166	-60°.4
18°	1.0145	-59°.6
27°.5	1.0107	-58°.0

A portion of the acid which was distilled under diminished pressure gave  $[\alpha]_D = -53°.9$ , indicating that distillation may cause the conversion of a part of the acid into the racemic form or into cistranscampholytic acid.

*$\beta$ -Bromdihydrocampholytic Acid*,  $C_5H_{11} \begin{matrix} \swarrow Br. \\ \searrow CO_2H \end{matrix}$ . — This was

prepared from the cistranscampholytic acid by putting 2 grams of the acid in a small glass-stoppered bottle, adding a little ligroin and 8-10 cc. of fuming hydrobromic acid, and shaking for a few minutes. Enough ligroin was then added to dissolve the brom acid, and the ligroin solution was separated and dried with sodium sulphate. The solution was then evaporated immediately in a vacuum desiccator by continuous evacuation. The crystals obtained were dissolved in cold ligroin and recrystallized in the same manner.

From the dihydrohydroxycampholytic acid the brom acid was prepared and crystallized in essentially the same manner.

The brom acid obtained from the cistranscampholytic acid gave, in a 10 per cent solution in benzene :

$$[\alpha]_D = +89°.6 \text{ and } 91°.5.$$

The brom acid obtained from the dihydrohydroxycampholytic acid gave, under the same conditions :

$$[\alpha]_D = +93° \text{ and } 94°.$$

While the agreement is not exact, when we consider the ease with which cistranscampholytic acid passes over into cis-campholytic acid when treated with mineral acids, and, further, that the compound was prepared in the first case from a body with a negative rotation of 59°, and in the second case from one with a positive rotation of 72°, there seems to be no reasonable ground for doubting the identity of the acid from the two sources.

## A NEW METHOD FOR THE DETERMINATION OF ALUMINIUM.

BY E. T. ALLEN AND V. H. GOTTSCHALK.

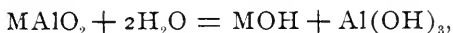
In the course of some experimental work requiring many determinations of aluminium, we became impressed with the tediousness of the ordinary method. Fortunately, the majority of cases where aluminium is to be determined involve its precipitation together with iron. The greater the proportion of iron the denser and more readily filtered is the precipitate, but when aluminium is unaccompanied by iron, and especially when the percentage is high, the slowness with which the precipitate settles, the difficulty involved in washing it completely, the small quantity which can be successfully handled at once, and the danger of loss by solution, all conspire to make the determination a troublesome one. We made some effort to improve the ammonia method, but without any very marked success.

We compared the precipitate formed by ammonia with that formed by other reagents; ammonium carbonate and ammonia, ammonium sulphide and ammonia, ammonium phosphate and ammonia, but it did not appear to us that any of the above possessed much advantage over ammonia and ammonium chloride. The precipitates by all the above reagents are as gelatinous and difficult to filter and wash as the hydroxide by ammonia. Of Löwe's<sup>1</sup> method, *viz.*, the precipitation of the aluminium from a soluble aluminate by ammonium chloride, we had greater hopes, but our experience with it was a disappointment. We find the precipitate little, if any, denser than that thrown down by ammonia, while the danger of extracting silica from the glass during the considerable time necessary to boil off the ammonia, together with the well-known capacity of alumina for precipitating such substances from solution, constitute an objection to this method.

In searching for a new method, we endeavored to find an insoluble compound of aluminium which could be formed by precipitation and which is also crystalline, admitting of rapid

<sup>1</sup> J. B., 1860, 132; Chem. Ztg., 3, 247.

and complete washing. The only compounds known to us which fulfilled these conditions are the crystalline hydroxide and the basic carbonate. The former is only precipitated from a soluble aluminate by the action of water :



and this reaction is not sufficiently complete for a quantitative method. We therefore turned our attention to the basic carbonate.

*Preliminary Experiments with the Basic Carbonate of Aluminium.*

In our first experiments we dissolved the substance in which the aluminium was to be determined in varying quantities of water, added just enough potash or soda to redissolve the precipitate at first formed, precipitated with carbon dioxide, and then washed in various ways.<sup>1</sup> We were especially struck with the ease and rapidity with which the precipitates could be washed. To test the filtrates for alumina, we boiled with hydrochloric acid to decompose carbonate, added ammonia and colorless ammonium sulphide, and allowed to stand. In every case where the action of the gas had been continued for a sufficient length of time, no more alumina could be obtained from the filtrates. The results were generally somewhat high, but the error in many cases was so small and so nearly constant that we suspected it might be due to impurities precipitated from the alkali. An examination of several different samples of "C. P." caustic potash and "C. P." caustic soda proved that all, not excepting "sodium hydrate from sodium" contained silica, iron, and alumina. These impurities were carefully estimated as follows : About 20 grams of substance was weighed out of a closed flask, dissolved by distilled water, acidified, and evaporated with pure hydrochloric acid. The evaporation was performed in a platinum basin just as in an ordinary silica determination. The insoluble residue consisted of silicates, not pure silica. The filtrate was again evaporated in platinum, and in the residue the alumina and

<sup>1</sup> A little of the precipitate adheres tenaciously to the glass. This we dissolved in hot concentrated hydrochloric acid, precipitated with ammonia, and washed on a separate filter. According to the conditions which we finally adopted (p. 302), the precipitate is boiled with water. It can then be removed entirely, without acid.

iron were determined as usual. For most of our work we selected a potash containing 0.05 per cent of the above-mentioned impurities. A considerable quantity of it was put into a glass-stoppered bottle of wide mouth and kept in the solid state. In our subsequent experiments we used weighed quantities of this potash, calculated the weight of the impurities, and assuming<sup>1</sup> that they were entirely precipitated with the alumina, subtracted the same from the weight of the precipitates. We chose "C. P." ammonium alum and "C. P." aluminium metal as the substances best adapted for a test of the method. The alum was carefully recrystallized and thoroughly dried in a desiccator over calcium chloride. Tested in a color cylinder, with potassium sulphocyanate, it showed no trace of iron. Below are given our results with ammonium alum, in which a correction was made for impurities in the potash. All the results are given without reserve :

*Preliminary Determinations of Aluminium in Ammonium Alum.*

	Alum taken. Grams.	Al <sub>2</sub> O <sub>3</sub> found. Gram.	Al <sub>2</sub> O <sub>3</sub> calculated. Gram.	Difference. Milligrams.
1	1.2144	0.13737	0.13686	+0.51
2	1.0289	0.11737	0.11596	+1.41
3	1.1111	0.12550	0.12522	+0.28
4	0.9314	0.10530	0.10497	+0.33
5	1.4191	0.15921	0.15993	-0.72
6	1.1545	0.12911	0.13011	-1.00
7	1.1632	0.12966	0.13109	-1.43
8	1.3483	0.15230	0.15195	+0.35
9	1.2818	0.14460	0.14446	+0.14
10	1.6831	0.18796	0.18969	-1.73
11	1.1086	0.12648	0.12494	+1.54
12	1.0359	0.11881	0.11675	+2.06
13	1.1651	0.13229	0.13131	+0.98
14	1.0164	0.11548	0.11455	+0.93
15	1.1964	0.13482	0.13483	-0.01
16	1.1256	0.12272	0.12686	-4.14

A few of the results are decidedly low, owing probably to a slight solvent action of the wash-water, an error which we found later could be effectually guarded against. A still greater number are slightly high. The results with metallic

<sup>1</sup> See page 295.



aluminium were still higher. We suspected the cause to be alkali in the precipitates, an impurity which our method of washing had not sufficed to remove. Taken as a whole, however, the results appeared sufficiently encouraging to justify a further study of the method.

*The Completeness of Precipitation.*

As previously stated, our preliminary experiments showed that the filtrates from the precipitates by carbonic acid, when they were boiled with hydrochloric acid and then treated with ammonia and ammonium sulphide, yielded not the slightest precipitate. We now subjected the filtrates to a more rigid test, by evaporating the same to dryness with pure hydrochloric acid in a platinum basin, taking up the residue in a little boiling water, precipitating with ammonia, filtering, washing thoroughly, igniting in a tared platinum crucible, and weighing the insoluble residue. The results are given below :

Filtrate.		Gram.
1	Precipitate by ammonia, less ash	0.00021
2	" " " " " "	0.00051
3	" " " " " "	0.00061
Average,		0.00044

Each of these filtrates had a volume of about 0.5 liter. Now, the average of three determinations showed us that our distilled water contained 0.00046 gram residue per 0.5 liter, a portion of which, in the above-mentioned operation, would appear as "insoluble" residue. We therefore conclude that not only is the alumina completely precipitated but also the impurities in the potash ; *viz.*, iron, alumina, and silica.

*Solubility of the Basic Carbonate of Aluminium.*

This was determined by preparing some of the substance as in an ordinary analytical determination, washing thoroughly with cold water, shaking up with distilled water, and allowing it to stand for a week or more at nearly constant temperature, filtering out 1 liter of the solution into a dry measuring flask, evaporating to dryness in a platinum basin, and finally transferring to, and evaporating in a weighed platinum cruci-

ble. A blank with distilled water was carried out under the same conditions. To guard against imperfect washing, the process was repeated with the same material until the results were constant :

		Gram.
1st det.	1 liter of solution at 20° C. contained	0.0025
	Blank	0.0011
		<hr/>
		0.0014
2nd det.	1 liter of solution at 20° C. contained	0.0025
	Blank	0.0012
		<hr/>
		0.0013

This substance is not a perfectly pure compound, as the sequel shows. Besides, when heated to redness it loses about 5 per cent of carbon dioxide. The above results, therefore, have no value as determinations of a physical constant, but they suffice to show that even in pure water the substance is practically insoluble—much less soluble, for example, than barium sulphate.

#### *Composition of the Precipitate.*

The precipitate which carbon dioxide throws down from a soluble aluminate has generally been assumed to be crystalline hydroxide, though Day<sup>1</sup> has shown it to be a basic carbonate. He prepared and analyzed a large number of preparations, but his conditions varied from ours in that his aluminate solutions must have contained an excess of alkali. He found that the substance always contained carbon dioxide and alkali though the percentages varied widely. We find that when potash is added to an aluminium solution, in quantity just sufficient to redissolve the precipitate which first forms, carbon dioxide acts on the aluminate with the formation of an insoluble substance of nearly constant composition. The following preparations were precipitated from solutions of various concentrations (1 gram  $\text{Al}_2\text{O}_3$  : 1500 cc.  $\text{H}_2\text{O}$  to 1 gram  $\text{Al}_2\text{O}_3$  : 3000 cc.  $\text{H}_2\text{O}$ ), washed with cold water and air-dried.

<sup>1</sup> This JOURNAL, 19, 707 (1897).

*Analyses of Basic Carbonate of Aluminium.*

- I. 0.2144 gram substance gave 0.1092 gram  $\text{Al}_2\text{O}_3$  and 0.0027 gram  $\text{K}_2\text{SO}_4$ .  
 0.3813 gram substance lost 0.1825 gram on ignition.  
 0.8480 gram substance gave 0.3503 gram  $\text{H}_2\text{O}$  and 0.0438 gram  $\text{CO}_2$ .
- II. 0.7440 gram substance gave 0.3144 gram  $\text{H}_2\text{O}$  and 0.043 gram  $\text{CO}_2$ .
- III. 0.1996 gram substance gave 0.09975 gram  $\text{Al}_2\text{O}_3$ .
- IV. 0.5802 gram substance lost, on ignition, 0.2882 gram.  
 0.5707 gram substance gave 0.2388 gram  $\text{H}_2\text{O}$  and 0.0267 gram  $\text{CO}_2$ .  
 0.3900 gram substance gave 0.1960 gram  $\text{Al}_2\text{O}_3$  and 0.0026 gram  $\text{K}_2\text{SO}_4$ .
- V. 0.1995 gram substance gave 0.09954 gram  $\text{Al}_2\text{O}_3$ .

	Calculated for $4\text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 20\text{H}_2\text{O}$ or $\text{Al}(\text{OH})\text{CO}_3 \cdot 7\text{Al}(\text{OH})_3 \cdot 9\text{H}_2\text{O}$ .	I.	II.	Found. III.	IV.	V.
$\text{H}_2\text{O}$	44.29	41.31 <sup>1</sup>	42.26 <sup>1</sup>	....	41.84 <sup>1</sup>	....
$\text{CO}_2$	5.41	5.17	5.78	....	4.68	....
Loss on ignition	49.70	47.87	....	....	49.68	....
$\text{Al}_2\text{O}_3$	50.30	50.94	....	49.98	50.26	49.90
$\text{K}_2\text{O}$	....	0.68	....	....	0.36	....

The water and carbon dioxide were determined by heating the substance in a hard glass tube as high as possible and collecting in sulphuric acid and caustic potash, respectively. The alumina was carefully precipitated from a hydrochloric acid solution of the substance by means of ammonia. The filtrate was then evaporated in platinum and the residue treated with water and a little ammonia to recover traces of alumina, after which the second filtrate was again carried to dryness, also in platinum. The residue was then transferred to a large platinum crucible, from which the ammonium salts were driven at a low red heat. The residue was now treated with a few drops of pure sulphuric acid, and heated to redness again. Finally, to guard against the formation of acid sulphate, the residue was heated a third time with pure ammonium carbonate. From the weight of the potassium sulphate

<sup>1</sup> The results for water are probably all low except perhaps in I. We had no platinum tube at our disposal, and we did not succeed in getting a sufficient temperature, using a glass tube.

thus obtained, the residue obtained in a blank was subtracted. The quantity of potash is evidently too small to be regarded as an essential constituent. A small quantity of carbonate or acid carbonate is probably held in the substance by capillary attraction. The experiments of Day show that this compound possesses an unusual capacity for absorption. If we consider the reduction of percentages produced by the impurity and also the error to which the water determinations were subject, the numbers are seen to agree well with a fairly simple formula, *viz.*,  $\text{Al}(\text{OH})\text{CO}_3 \cdot 7\text{Al}(\text{OH})_3 \cdot 9\text{H}_2\text{O}$ .

*Decomposition of the Basic Carbonate of Aluminium by Water.*

We found that when the carbonate was treated with boiling water it underwent a decided change in appearance, becoming flaky and apparently amorphous. This change of state marks a change in composition, the basic carbonate loses carbon dioxide, water, and alkali, and becomes the hydroxide,  $\text{Al}(\text{OH})_3$ . The gas evolved in the decomposition carries the flakes of the precipitate to the top of the liquid and for a time prevents rapid settling. The following are analyses of preparations boiled with six and eight successive portions of water, respectively, and air-dried :

I. Boiled with water six times :

0.3461 gram substance gave 0.2284 gram  $\text{Al}_2\text{O}_3$  and 0.0023 gram  $\text{K}_2\text{SO}_4$ .

0.3353 gram substance lost, on ignition, 0.1146 gram.

	Calculated for $\text{Al}(\text{OH})_3$ .	Found.
$\text{Al}_2\text{O}_3$	65.43	65.99
$\text{H}_2\text{O}$	34.57	34.18
$\text{K}_2\text{O}$	0.00	0.36
		<hr/> 100.53

II. Boiled with water eight times :

0.2393 gram substance gave 0.1571 gram  $\text{Al}_2\text{O}_3$  and no  $\text{K}_2\text{SO}_4$ .

0.4755 gram substance lost, on ignition, 0.1642 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{Al}(\text{OH})_3$ .	Found.
$\text{Al}_2\text{O}_3$	65.43	65.65
$\text{H}_2\text{O}$	34.57	34.53
$\text{K}_2\text{O}$	0.00	0.00
		<hr/> 100.18

It seemed altogether probable that the alkali might be removed more rapidly by boiling the preparation with water containing a little chloride or nitrate of ammonium. This we found to be the case.

III. Basic carbonate of aluminium, after boiling with three successive portions of water containing a little ammonium nitrate. Air-dried.

0.5292 gram substance lost, on ignition, 0.1810 gram.

0.3454 gram substance gave 0.2292 gram  $\text{Al}_2\text{O}_3$  and no  $\text{K}_2\text{SO}_4$ .

	Calculated for $\text{Al}(\text{OH})_3$ .	Found.
$\text{Al}_2\text{O}_3$	65.43	66.36
$\text{H}_2\text{O}$	34.57	34.20
$\text{K}_2\text{O}$	0.00	0.00
		<hr/> 100.56

In our first determinations we avoided boiling the precipitate, and sought for conditions under which the alkali could be removed without changing its dense character.

Our results showed that this could be done with ammonium alum. The higher results which we obtained with other substances were probably due in part to the absence of ammonium salts, which, in case of the alum, decomposed the potassium carbonate retained by the precipitate during the washing with hot water, thus:



The potassium sulphate formed is more readily removed.

*Properties of Aluminium Hydroxide Formed from the Basic Carbonate.*

Fortunately, we found the hydroxide formed in this way much denser than the ordinary variety. It still filtered rapidly and was so compact that we found no difficulty in washing 0.350 gram on a 9 cm. filter-paper. The precipitate does not always settle well after it has been boiled several times with water, but it still washes rapidly with the aid of the pump. The addition of the ammonium salt not only removes the alkali as explained above, but it prevents the solution of

alumina to which this variety of hydroxide is as liable as any other. Finally, though we wash on the filter with pure water, we have proved by experiment that, even when a considerable quantity of ammonium chloride remains in the precipitate, the weight of alumina which is volatilized on ignition is almost inappreciable. Theoretically, ammonium nitrate should be better than ammonium chloride, and practically, both work well.

*Ignition.*—Aluminium hydroxide, as is well known, requires the highest heat of the blast-lamp for complete dehydration. Handy<sup>1</sup> states that the resulting oxide is very hygroscopic. Our results accord with his. As such substances sometimes become denser and less hygroscopic at higher temperatures, and as Fresenius and other authorities on quantitative analysis do not mention this property of aluminic oxide, we concluded to try the effects of a higher heat. Platinum crucibles containing precipitates which had been heated for ten minutes in the blast-lamp, were set on an unglazed porcelain tile inside the muffle of a Hoskin's gasoline furnace. The maximum temperature reached was 1150° C. as measured by the electromotive force of a platinum-rhodium couple. The precipitates were kept for half an hour at this temperature, but after cooling they were as hygroscopic as ever.

*Weighing.*—All crucibles were heated in a blast-lamp and cooled for from ten to fifteen minutes in a sulphuric acid desiccator. The weight was then taken quickly, after which the crucible was again heated and cooled as before. The weights were now placed in the pan and the rider in the position it occupied during the first weighing. Then the crucible was quickly placed in the other pan and its weight estimated from the first swing of the beam. The weight of the crucible with the precipitate was taken under exactly the same conditions as that of the empty crucible. We employed a set of weights which we had carefully corrected.

*Results on "C. P." Aluminium.*—We first carefully determined the impurities of the metal as follows: The estimation of total silicon was made according to the method given by

<sup>1</sup> J. Am. Chem. Soc., 18, 768.

Handy.<sup>1</sup> The iron was determined colorimetrically. The standard solution was made from pure ferric chloride. The iron in it was determined by precipitation with ammonia. A carefully weighed quantity of metallic aluminium was then dissolved in pure hydrochloric acid, oxidized by pure chlorine water, and diluted to a measured volume.<sup>2</sup> A measured volume of the solution was then run into a Nessler cylinder, diluted to 50 cc. and treated with 2 cc. of a 10 per cent solution of potassium sulphocyanate. The tint it gave was matched by that of a measured volume of the standard under the same conditions.

Metal I. 1.0403 grams substance gave 0.0083 gram  $\text{SiO}_2$ .  
1.0037 grams dissolved in HCl was diluted to 250 cc.  
10 cc. of this solution matched the tint given by  
1.2 cc. standard. 1 cc. standard contained  
0.0313 mg. Fe.

Metal II. 1.1878 grams substance gave 0.0142 gram  $\text{SiO}_2$ .  
1.0009 grams were dissolved, oxidized, and diluted  
to 500 cc. 5 cc. of this solution = 1.4 cc.  
standard.

	I.	II.
Si	0.37	0.56
Fe	0.094	0.44
Al (diff.)	99.536	99.00

A consideration of the methods used, as well as a careful repetition of our analyses, convinced us that our results were correct within a few hundredths of 1 per cent. As silicon and iron were the only impurities found, we subtracted the sum of these from 100 per cent and called the difference aluminium. Standard solutions of these two samples were prepared by dissolving known weights in pure hydrochloric acid and oxidizing with pure chlorine. When the excess had been boiled out the solutions were very carefully filtered from the finely divided silicon and diluted to 500 cc.

The concentrations of these are given below :

<sup>1</sup> J. Am. Chem. Soc., 18, 768.

<sup>2</sup> We observed that the very dilute solution of ferric chloride, which at first showed no trace of ferrous iron, became reduced on standing. The addition of chlorine water does not interfere with the sulphocyanate test.

Solution A. 1.0023 grams metal I in 500 cc.

" B. 1.0009 " " II " " "

" C. 1.0089 " " III " " "

The determinations of aluminium in these solutions were carried out as previously explained. 50 cc. were used for each. The table which follows for the most part explains itself. In the column under "calculated" are found the numbers calculated from the percentages of iron, and the percentages of aluminium obtained by difference :

cc. Volume taken.	Solution.	KOH used.	Imp. in KOH + filter ash.	Weight of precipitate found.	$Al_2O_3 + Fe_2O_3$ found.	$Al_2O_3 + Fe_2O_3$ calculated.	Difference.
50	A	1.563	0.00104	0.18939	0.18835	0.18825	+0.10
50	A	1.697	0.00111	0.18953	0.18842	0.18825	+0.17
50	B	1.653	0.00109	0.18853	0.18744	0.18747	-0.03
50	B	1.630	0.00107	0.18808	0.18701	0.18747	-0.46
50	B	1.630	0.00107	0.18853	0.18746	0.18747	-0.01
50	B	1.530	0.00101	0.18780	0.18679	0.18747	-0.68
50	A	1.848	0.00146	0.19033	0.18887	0.18825	+0.62
50	A	1.993	0.00152	0.19028	0.18876	0.18825	+0.51
50	B	2.022	0.00155	0.18959	0.18804	0.18747	+0.57
50	B	2.022	0.00155	0.18910	0.18755	0.18747	+0.08
50	C	1.930	0.00132	0.19048	0.18916	0.18897	+0.19
50	C	1.930	0.00132	0.19078	0.18946	0.18897	+0.49
Average,							+0.13

#### *Detailed Directions for the Method.*

Dissolve the substance in which the aluminium is to be determined in water or a mineral acid. In case the latter is used, nearly neutralize with ammonia. Now dissolve a stick of potash in which the silica, iron, and alumina are known, in a measured quantity of water, and mix thoroughly. 1-2 grams of potash should be sufficient. Pour the potash solution into a burette, and from thence introduce into the aluminium solution a quantity of the former, sufficient to redissolve the precipitate which first forms. If the solution is still turbid no harm is done, but any considerable excess of potash should be



avoided. We have also used soda and, so far as our experience goes, it may be used as well as potash. Now pass a stream of carbon dioxide into the solution. If the alkali is not in too great excess, precipitation begins in a minute or two. Twenty minutes should suffice to precipitate 0.200 gram  $\text{Al}_2\text{O}_3$ . In testing the method we usually allowed the precipitate to settle completely or nearly so, but the bulk of the alumina comes down in a few minutes, and filtration then proceeds without difficulty. Transfer the precipitate for the most part to a 9 cm. filter and wash several times without suction. The soluble impurities are now mostly removed. Break the paper with a stirring rod, wash back completely into the original beaker, and boil the precipitate a few minutes with about 150–200 cc. water containing a little pure ammonium chloride or nitrate. The boiling should be continued only two or three minutes, otherwise the precipitate does not settle well. As soon as it has settled, pass the supernatant liquid through a new filter, using this time a pump and cone. Repeat the boiling and decantation once or twice, transfer the precipitate to the filter, and wash several times with hot water. Suck dry and transfer to a covered crucible, which has been weighed as directed previously. Dry carefully over the flame, burn the paper,<sup>1</sup> and heat from five to ten minutes at the highest temperature of the blast-lamp. Cool from ten to fifteen minutes in a sulphuric acid desiccator, and make an approximate weighing. Heat again for five minutes, cool as before, and weigh as directed. From the weight of the precipitate subtract the weight of the impurities in the potash.<sup>2</sup>

### *Summary.*

1. The precipitate which carbonic acid throws down from sodium or potassium aluminate is a basic carbonate of aluminium containing small amounts of alkaline carbonate. The latter may be effectually removed by boiling with water containing a little ammonium chloride or nitrate. At the same time the precipitate changes to the hydroxide,  $\text{Al}(\text{OH})_3$ . The

<sup>1</sup> Of course this means both filters.

<sup>2</sup> In technical work where the greatest accuracy is not required, one may easily omit weighing the potash after a little experience. Generally the impurities amount to about 0.001 gram in C. P. potash.

silica, iron, and alumina in the alkali come down with the precipitate.

2. We find the aluminium hydroxide prepared as above is dense and filters rapidly. 0.350 gram can be washed with far less difficulty than 0.050 gram precipitated by ammonia. It is so compact that the above weight may be washed without trouble on a 9 cm. paper.

3. Parallel determinations show that this method is much more rapid than the old one, while the results can be uniformly depended on.

4. It is accurate in the presence of sulphates, while the old method under this condition gives high results.

5. The method is as accurate as the old one for iron and alumina together, and, where the proportion of the latter is large, may be used to advantage. In the presence of the alkaline earths and lithium the method is not applicable. It is especially adapted to the determination of aluminium in samples of the metal, in certain alloys, the alums, hydroxides, etc., substances which give the most trouble in the precipitation by ammonia. If barium is present, of course it may be removed by sulphuric acid, when the alumina may be precipitated in the filtrate after nearly neutralizing with ammonia.

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## THE ACTION OF CAUSTIC HYDROXIDES ON ALUMINIUM.

BY E. T. ALLEN AND H. F. ROGERS.

It is commonly stated in text-books that aluminium dissolves in caustic alkalies with the evolution of hydrogen and the formation of aluminates, but the latter products of the reaction have been little studied. Cavazzi<sup>1</sup> has investigated the action of sodium and potassium hydroxides on aluminium, and concludes that the soluble salts formed belong to the same type as the natural aluminates, *viz.*,  $\text{MAIO}_2$ .

We have further examined these reactions and also the action of lithium, barium, strontium, and calcium hydroxides. These reagents all exert a decided action on the metal even

<sup>1</sup> Gazz. chim. ital., 15, 202 (1885).

in the cold. The products belong to several different types according to the chemical nature of the hydroxide and the conditions of experiment. The samples of aluminium we used in our work were the so-called "C. P." metal of the market. Their composition follows :

	I.	II.
Al	99.41	99.64 (by diff.)
Fe	0.05	0.02
Si	0.42	0.34
	<hr/>	<hr/>
	99.88	100.00

*I. Action of Potassium Hydroxide.*

A solution of 4.5 grams of caustic potash in 45 cc. water was poured into a large silver crucible, and to it was added sheet aluminium cut into small pieces. Effervescence began immediately, the temperature rose from the heat evolved, and at 60° C. the reaction was vigorous. After some time and while the action was still strong, a white crystalline precipitate began to separate. This soon formed, on the surface of the metal and on the sides of the vessel, a hard, porcelain-like layer, difficult to remove. A portion of this product was washed with alcohol and dried in the sun.

I. 0.5194 gram substance gave 0.1804 gram  $\text{H}_2\text{O}$ .

0.1597 gram substance gave 0.1053 gram  $\text{Al}_2\text{O}_3$ .

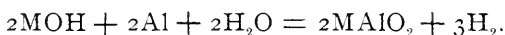
II. 0.4252 gram substance gave 0.1430 gram  $\text{H}_2\text{O}$ .

0.3469 gram substance gave 0.2257 gram  $\text{Al}_2\text{O}_3$ .

	Calculated for $\text{Al}(\text{OH})_3$ .	I.	Found.	II.
$\text{H}_2\text{O}$	34.57	34.73		33.64
$\text{Al}_2\text{O}_3$	65.43	65.93		65.06

The product was therefore crystalline aluminium hydroxide. To decide whether this was formed through the agency of the carbon dioxide of the air, we repeated the experiment, using a glass flask instead of the crucible. The reaction mixture was protected from the air by a stream of hydrogen which had been previously washed by caustic soda. The result was the same. The hydroxide was therefore due to the action of water on the dissolved aluminate.

Cavazzi<sup>1</sup> states that the alkalies dissolve aluminium in the proportion demanded by the equation :



We repeated his experiments, using 4.5 grams of potash in 45 cc. water. The reaction did not appear to slacken until hydrolysis set in, when the surface of the metal became rapidly coated with aluminium hydroxide. On the addition of fresh metal the reaction progressed vigorously, and was so continued until we were satisfied that as long as the water was replenished and a fresh metallic surface exposed, aluminium would continue to evolve hydrogen and form hydroxide. At the end of the experiment the pieces of metal which remained were cleaned, dried, and weighed. 6.9 grams had been consumed, whereas, 4.5 grams of potash, according to Cavazzi, should dissolve 2.17 grams metal.

Cavazzi appears to have used a more dilute solution than the above (1 gram KOH : 20 cc.  $\text{H}_2\text{O}$ ), but mentions no decomposition. He considered the equivalency of aluminium and potash an argument for the composition of the product. He also evaporated the solution of the metal to dryness, obtaining a gummy mass which contained for 39.1 parts of potassium, 26.55 parts of aluminium.

*Potassium Aluminate*,  $\text{K}_2\text{Al}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ .—In accord with the principle of mass action, hydrolysis of the aluminate does not take place when the potash is in considerable excess. Seven grams potash in 70 cc. water was used to dissolve 2.25 grams metal. The solution was filtered from silicon and set away in a vacuum desiccator over sulphuric acid. When the liquid had become quite syrupy, hard, wart-like, crystalline aggregates appeared. The microscope showed them to consist of transparent tables. They were separated from the solution mechanically, washed, and then repeatedly ground in a mortar with alcohol which had been distilled over lime. The snow-white crystalline powder was then dried over sulphuric acid *in vacuo*.

0.4155 gram substance gave 0.0907 gram  $\text{H}_2\text{O}$ .

0.2199 gram substance gave 0.0885 gram  $\text{Al}_2\text{O}_3$ .

<sup>1</sup> Gazz. chim. ital., 15, 202.

	Calculated for $K_2Al_2O_4 \cdot 3H_2O$ .	Found.
$K_2O$ (diff.)	37.63	37.93
$H_2O$	21.56	21.82
$Al_2O_3$	40.80	40.25

Potassium aluminate is insoluble in alcohol, soluble in water only with partial decomposition into free potash and amorphous aluminium hydroxide, even when an extremely small quantity of solvent is used. It is hygroscopic and sensitive to carbonic acid. The same substance was long ago obtained by Fremy<sup>1</sup> by dissolving alumina in potash. We are able to verify all his statements concerning it except its complete solubility in water.

In the reaction between potash and aluminium, an excess of the latter makes no difference except that a certain quantity is, of course, necessary to effect hydrolysis, but no acid salt was obtained. By the use of a large excess of potash an attempt was made to isolate a derivative of the normal aluminium hydroxide, but without success. 1.12 grams metal were dissolved in 7 grams potash and 50 cc. water. The ratio  $3KOH : Al$  demands 6.96 grams potash for 1.12 grams metal. After the solution had evaporated for several days *in vacuo*, both its upper and lower surfaces were found encrusted with crystals. Alcohol did not change their appearance.

0.4329 gram substance gave 0.0949 gram  $H_2O$ .

	Calculated for $K_2Al_2O_4 \cdot 3H_2O$ .	Found.
$H_2O$	21.56	21.92

## II. Action of Sodium Hydroxide.

Sodium hydroxide exerts on aluminium an action analogous to that of potash. It is decided at ordinary temperatures, and, as the temperature rises, becomes vigorous or violent according to the strength of the soda solution. But even in strong solutions, when the quantity of metal is that required by the ratio  $Al : NaOH$ , hydrolysis invariably takes place. Cavazzi<sup>2</sup> took 1 gram caustic soda in 20 cc. water, dissolved by its aid 0.6775 gram aluminium, evaporated the solution to dryness, and subjected the residue to analysis. He states

<sup>1</sup> Ann. chim. phys. [3], 12, 362.

<sup>2</sup> Gazz. chim. ital., 15, 202.

that it contained 23 parts of sodium to 26.11 parts of aluminium. This agrees well with the formula  $\text{NaAlO}_2$ , but in view of the fact that we always observed hydrolysis under such conditions as those above specified, and since sodium aluminate requires a high temperature for dehydration, Cavazzi's preparation must have been, at least in part, the product of several reactions. We, therefore, considered it worth while to attempt the isolation of the aluminate by a process involving no secondary reactions. Sodium aluminate is described by Fremy and Cavazzi as a gummy mass. We could not bring a solution of it to crystallization by evaporation *in vacuo*. In one case we dissolved 2 grams of aluminium in 5 grams caustic soda contained in 50 cc. water. With such an excess of alkali no alumina separates. The filtered solution was evaporated *in vacuo* to a thick colorless syrup. This syrup was spread on a porous tile and then kept *in vacuo* over sulphuric acid and phosphorus pentoxide for some weeks without any sign of crystallization. When the syrup is rubbed in a mortar with successive portions of alcohol it assumes the consistency of candied sugar. If this product is then boiled repeatedly with alcohol it loses water and soda, and on cooling becomes hard. It may now be ground with cold alcohol into a powder and dried in a vacuum desiccator. Most of the free soda is extracted by alcohol without difficulty, but the last portion of 2 or 3 per cent apparently cannot be removed by alcohol which has been distilled over lime. Ninety-five per cent alcohol removes it, but if its action is long continued hydrolysis will take place. The following are analyses of two preparations made by the above method:<sup>1</sup>

- I. 0.2040 gram substance gave 0.0601 gram  $\text{H}_2\text{O}$ .  
       0.1971 gram substance gave 0.0876 gram  $\text{Al}_2\text{O}_3$ .
- II. 0.3399 gram substance gave 0.0999 gram  $\text{H}_2\text{O}$ .  
       0.2992 gram substance gave 0.1249 gram  $\text{Al}_2\text{O}_3$ .

	Calculated for $\text{Na}_2\text{Al}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ .	I.	Found. II.
$\text{H}_2\text{O}$	30.49	29.46	29.39
$\text{Al}_2\text{O}_3$	43.26	44.46	41.75
$\text{Na}_2\text{O}$ (diff.)	26.25	26.08	28.86

<sup>1</sup> To avoid the presence of sodium carbonate in the final product, the soda solution used to dissolve the aluminium was boiled with a small lump of lime, and filtered.

I.  $\text{Al}_2\text{O}_3 : \text{Na}_2\text{O} : \text{H}_2\text{O} = 1 : 0.967 : 3.763$ .

II.  $\text{Al}_2\text{O}_3 : \text{Na}_2\text{O} : \text{H}_2\text{O} = 1 : 1.14 : 4.00$ .

An attempt was made to isolate the compound  $\text{Na}_3\text{AlO}_3$ . Metallic aluminium was dissolved in the theoretical quantity of caustic soda, but no crystals were obtained from the solution in the vacuum desiccator. Tissier<sup>1</sup> claims to have prepared this compound by the action of lime on cryolite, but it should be noticed that the soluble products of the reaction were calcined at a red heat before analysis.

He obtained from the calcined substance 34.66 per cent alumina instead of 35.46 per cent demanded by  $\text{Na}_3\text{AlO}_3$ . We find no convincing evidence that  $\text{Na}_3\text{AlO}_3$ <sup>2</sup> can be formed in the wet way.

### III. Action of Lithium Hydroxide.

Caustic lithia reacts with aluminium quite vigorously. In a comparatively short time a precipitate separates which at first we judged to be aluminium hydroxide but which careful examination proved to be a difficultly soluble aluminate. A number of preparations were made. The following conditions gave good results :

Four grams of lithium hydroxide is dissolved in 75 cc. water, boiled a minute or two with a small lump of pure lime to precipitate carbonate, and quickly filtered into a round-bottomed flask of 250 cc. capacity. Several grams of aluminium in small pieces are now added and the flask stoppered with a rubber stopper provided with a Bunsen valve. As soon as a considerable precipitate has formed it is quickly filtered, washed rapidly several times with cold water, followed by alcohol, and finally ether. It may be dried over calcium chloride or air-dried in the sun, provided it is not too long exposed. The following preparations were made under the same or slightly differing conditions.

I. 0.2047 gram substance gave 0.0944 gram  $\text{H}_2\text{O}$ .

0.1264 gram substance gave 0.0593 gram  $\text{Al}_2\text{O}_3$ .

II. 0.2451 gram substance gave 0.1121 gram  $\text{H}_2\text{O}$ .

0.1768 gram substance gave 0.0835 gram  $\text{Al}_2\text{O}_3$ .

<sup>1</sup> C. R., 43, 102.

<sup>2</sup> The statement of Graham-Otto, Vol. IV., Part 1, p. 90, regarding  $\text{Na}_3\text{AlO}_3$  is evidently an error.

III. 0.2588 gram substance gave 0.1194 gram  $\text{H}_2\text{O}$ .  
 0.1984 gram substance gave 0.0944 gram  $\text{Al}_2\text{O}_3$ .

	Calculated for $\text{LiH}(\text{AlO}_2)_2 \cdot 5\text{H}_2\text{O}$ .	I.	Found. II.	III.
$\text{H}_2\text{O}$	45.80	46.11	45.73	46.15
$\text{Al}_2\text{O}_3$	47.27	46.91	47.23	47.47
$\text{Li}_2\text{O}$ (diff.)	6.93	6.98	7.04	6.38

Heated in a stream of pure dry hydrogen, 1.7635 grams at  $100^\circ\text{C}$ . lost 0.1399 gram, = 7.94 per cent.

A loss of 1 mol.  $\text{H}_2\text{O}$  from  $\text{LiH}(\text{AlO}_2)_2 \cdot 5\text{H}_2\text{O}$  = 8.32 per cent.

1.7884 grams at  $200^\circ\text{C}$ . lost 0.6040 gram = 33.78 per cent.

A loss of 4 mols.  $\text{H}_2\text{O}$  from  $\text{LiH}(\text{AlO}_2)_2 \cdot 5\text{H}_2\text{O}$  = 33.31 per cent.

2.3705 grams at  $275^\circ\text{C}$ . lost 0.9600 gram = 40.50 per cent.

A loss of 5 mols.  $\text{H}_2\text{O}$  from  $\text{LiH}(\text{AlO}_2)_2 \cdot 5\text{H}_2\text{O}$  = 41.62 per cent.

In a vacuum desiccator over sulphuric acid one preparation had not reached equilibrium after several months.

Another preparation, which stood two weeks over sulphuric acid *in vacuo* during hot weather, had the composition  $\text{LiH}(\text{AlO}_2)_2 \cdot 3\text{H}_2\text{O}$ .

0.1803 gram substance gave 0.0637 gram  $\text{H}_2\text{O}$ .

0.1621 gram substance gave 0.0917 gram  $\text{Al}_2\text{O}_3$ .

	Calculated for $\text{LiH}(\text{AlO}_2)_2 \cdot 3\text{H}_2\text{O}$ .	Found.
$\text{H}_2\text{O}$	34.96	35.33
$\text{Al}_2\text{O}_3$	56.72	56.57

*Lithium aluminate* is a light, white, coarsely granular substance. Under the microscope it is found to consist of very minute, wart-like clusters of crystals. It is much more stable toward water than the soluble aluminates of potassium and sodium. It may be washed repeatedly with cold water in which it is slightly soluble, but by boiling water it is slowly decomposed, though not greatly changed in appearance. After boiling one hour with successive portions of water, one preparation contained but 2 per cent lithia instead of 6.98 per cent. If, during the preparation of lithium aluminate, the solution is quickly filtered before much precipitation takes



place, it solidifies in a few minutes to a voluminous, soapy substance of the same composition as the precipitate. It cannot, however, be again dissolved by heating either with water or a solution of lithium hydroxide, except in very small quantities. Thus we have here a solution which seems to be super-saturated. It will be noticed that this compound belongs to a new type of aluminates,  $MH(AlO_2)_2$ . We were unable to obtain any other aluminate of lithium.

### III. Action of Barium Hydroxide.<sup>1</sup>

A hot concentrated solution of this base was first tried. Its action is vigorous in the beginning, but soon slackens, owing to the formation of a protective layer of aluminate on the surface of the metal. 30 to 40 grams of crystallized barium hydroxide was dissolved in 75 cc. hot water and filtered into a 250 cc. flask. The aluminium in small strips was now added and the flask was closed by a stopper with a Bunsen valve. A low flame kept the contents of the flask near the boiling-point. More metal was introduced from time to time until enough of the product for examination had formed. Most of it adhered tenaciously to the glass and metal. It was decidedly heavy, coarsely crystalline, somewhat soluble in water and decomposed by it. Under the microscope, comparatively large, transparent, monoclinic tables were observed. We found it so unstable as to require rapid and careful washing. Several preparations were largely decomposed by too long contact with water. The excess of baryta may be removed by washing rapidly two or three times with cold water, using the pump. The crystals should then be washed with alcohol and dried a short time over sulphuric acid.

- I. 0.4373 gram substance gave 0.0790 gram  $H_2O$ .  
0.2835 gram substance gave 0.2633 gram  $BaSO_4$ .
- II. 0.2059 gram substance gave 0.0353 gram  $H_2O$ .  
0.2358 gram substance gave 0.2247 gram  $BaSO_4$  and  
0.0464 gram  $Al_2O_3$ .

<sup>1</sup> Beckmann studied the action of this base on aluminium, but as his metal was quite impure and his solutions were dilute he isolated no product but  $Al(OH)_3$ . J. prakt. Chem., 26, 392 (1882).

	Calculated for $\text{Ba}_2\text{Al}_2\text{O}_6 \cdot 5\text{H}_2\text{O}$ .	I.	Found.	II.
$\text{H}_2\text{O}$	18.04	18.07		17.15
$\text{Al}_2\text{O}_3$	20.47	20.89 (diff.)		19.67
$\text{BaO}$	61.48	61.04		62.62

The same compound was obtained by Beckmann by the dissolving alumina in baryta water and crystallizing.<sup>1</sup> His observations agree with ours throughout.

In cold saturated baryta water containing an excess of undissolved crystals, aluminium dissolves rather slowly with the formation of an unstable amorphous(?) salt of a different type.

15 grams crystallized barium hydroxide was dissolved in 70 cc. hot water and filtered into a small Erlenmeyer flask, which was at once stoppered. The contents were then chilled by a jet of cold water, when most of the base crystallized out. The flask was then opened while a few pieces of metal were introduced, and again closed by a stopper with a Bunsen valve. A moderate evolution of hydrogen was observed, but the solution of the metal was comparatively slow. It depends on temperature, but is measured by days rather than hours. The crystals gradually passed into solution as the action proceeded and the product then gradually separated out. The product must be sucked off with the aid of pump and cone, and washed as rapidly as possible in the same way, first with water, then with 50 per cent alcohol, followed by concentrated alcohol. On account of the glutinous nature of the precipitate the operation is at best rather slow, so that the surface must be protected from the atmosphere. We carried out the washing in an apparatus swept by a current of air freed from carbon dioxide.

I. Washed once with cold water, several times with 50 per cent alcohol, and finally with 95 per cent alcohol. Dried a short time over sulphuric acid.

0.5452 gram substance gave 0.1502 gram  $\text{H}_2\text{O}$ .

0.2599 gram substance gave 0.1734 gram  $\text{BaSO}_4$ .

	Calculated for $\text{Ba}(\text{AlO}_2)_2 \cdot 5\text{H}_2\text{O}$ .	Found.
$\text{H}_2\text{O}$	26.05	27.54
$\text{BaO}$	44.39	43.84
$\text{Al}_2\text{O}_3$ (diff.)	29.57	28.62

$\text{Al}_2\text{O}_3 : \text{BaO} : \text{H}_2\text{O} = 1 : 1.02 : 5.46$ .

<sup>1</sup> J. prakt. Chem., 26, 398.

II. Washed twice with water, several times with 50 per cent alcohol, dried in air free from carbon dioxide, then over calcium chloride for some hours.

0.2387 gram substance gave 0.0645 gram  $\text{H}_2\text{O}$ .

0.2064 gram substance gave 0.1360 gram  $\text{BaSO}_4$ .

	Calculated for $\text{Ba}(\text{AlO}_3)_2 \cdot 5\text{H}_2\text{O}$ .	Found.
$\text{H}_2\text{O}$	26.05	27.02
$\text{BaO}$	44.39	43.30
$\text{Al}_2\text{O}_3$ (diff.)	29.57	29.68

$\text{Al}_2\text{O}_3 : \text{BaO} : \text{H}_2\text{O} = 1 : 0.972 : 5.17$ .

The compound is a soft, white powder, apparently amorphous, easily decomposed by water and by carbonic acid. Beckmann<sup>1</sup> obtained, in a different way, a barium aluminate of the same type containing 6-7 molecules of crystal water. The difference is doubtless due to the conditions of drying. After our experiments with strontia, to be described later, we tried the behavior of a cold saturated solution of baryta containing a very large excess of undissolved crystals, but the action, except that it was more rapid, appeared to be the same.

#### V. Action of Strontium Hydroxide.

When aluminium is boiled with a strong solution of strontium hydroxide hydrogen is liberated for a moment, after which there seems to be no further action. None of the other caustic hydroxides behaves similarly. When the metal is treated in the cold with a saturated solution of strontia containing an excess of solid crystals, a slight effervescence begins at once and continues. After some days the crystals pass into solution and a granular, sandy precipitate separates out. It is heavy, decidedly crystalline, and colored slightly brownish by the silicon of the metal.

The results of the analysis follow :

0.3269 gram substance gave 0.0659 gram  $\text{H}_2\text{O}$ .

0.2489 gram substance gave 0.0506 gram  $\text{Al}_2\text{O}_3$ .

	Calculated for $\text{Sr}_3(\text{AlO}_3)_2 \cdot 6\text{H}_2\text{O}$ .	Found.
$\text{H}_2\text{O}$	20.73	20.16
$\text{Al}_2\text{O}_3$	19.60	20.33
$\text{SrO}$ (diff.)	59.67	59.51

<sup>1</sup> J. prakt. Chem., 26, 406.

The same compound is thrown down in pure condition when a solution of potassium aluminate, containing an excess of potash, is poured into a hot solution of strontium chloride or hydroxide. The compound is then pure white, heavy, and more finely granular. These grains, when examined with the microscope, appeared to consist chiefly of dodecahedra. A considerable number of preparations were studied, and in every case these crystals were in the majority. The normal aluminate of strontium is one of the most stable aluminates. In cold water it is sparingly soluble. It may be washed repeatedly by the aid of a pump. On the other hand, samples which were washed by decantation, and remained longer in contact with water, were in large degree decomposed. The compound is stable over sulphuric acid and sensitive to carbonic acid. The following preparation was precipitated from a hot solution of strontium hydroxide, washed rapidly several times with cold water in air free from carbon dioxide, then with alcohol, and finally with ether.

0.4229 gram substance gave 0.0877 gram  $\text{H}_2\text{O}$ .

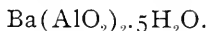
0.2676 gram substance gave 0.0519 gram  $\text{Al}_2\text{O}_3$ .

	Calculated for $\text{Sr}_3(\text{AlO}_3)_2 \cdot 6\text{H}_2\text{O}$ .	Found.
$\text{H}_2\text{O}$	20.73	20.74
$\text{Al}_2\text{O}_3$	19.60	19.40
$\text{SrO}$ (diff.)	59.67	59.86

The action of strontia on aluminium proceeds in two stages. The first stage, which has just been described, is complete when the strontia has passed into solution. In the second stage, the solution gradually becomes milky and a heavy amorphous precipitate forms. At the end of the first stage the solution is filtered from the normal aluminate. When a sufficient quantity of the second compound has separated from the solution it is filtered, washed, and dried. In appearance it closely resembles the aluminate of barium,  $\text{Ba}(\text{AlO}_2)_2 \cdot 5\text{H}_2\text{O}$ , but we have succeeded in preparing only one sample which was even approximately pure. All other preparations contained too little strontia, a circumstance which could be accounted for by hydrolysis.<sup>1</sup> The substance, being both finely

<sup>1</sup> On account of the previous separation of strontia in the form of  $\text{Sr}_3(\text{AlO}_3)_2$  the concentration of the base is considerably less than the baryta solution during the formation of  $\text{Ba}(\text{AlO}_2)_2$ .

divided and glutinous, is difficult to wash. The preparation, the analysis of which is given below, was made under practically the same conditions as the barium aluminate,



0.2329 gram substance gave 0.0629 gram  $\text{H}_2\text{O}$ .

0.2386 gram substance gave 0.0905 gram  $\text{Al}_2\text{O}_3$ .

	Found.
$\text{H}_2\text{O}$	27.01
$\text{Al}_2\text{O}_3$	37.93
$\text{SrO}$ (diff.)	35.06

$\text{SrO} : \text{Al}_2\text{O}_3 : \text{H}_2\text{O} = 1 : 1.1 : 4.44.$

#### VI. Action of Calcium Hydroxide.

When aluminium is added to lime-water no action is noted at first, but in a few minutes large bubbles of hydrogen begin to arise and, very slowly, the metal becomes coated with a white, crystalline layer. The reaction continues for many days. A number of preparations were thus made, but the composition of the products varied. This was probably due to the small concentration of lime-water and the opportunity thus afforded for the action of water. To remedy this difficulty and to prevent the formation of carbonate, a liter flask was filled with air free from carbon dioxide, which was then displaced by saturated lime-water. The flask was closed by a stopper with a Bunsen valve. From the stopper was suspended, by a string, a tube 5 cm. long and 2 cm. in diameter, containing several lumps of lime. Thus the water was kept saturated with the hydroxide throughout the experiment. Ten to fifteen grams of sheet aluminium were used in each experiment. After a number of days the liquid was siphoned off, the tube carefully removed, and the metal with its adherent layer washed with cold water, in an atmosphere free from carbon dioxide. It was then dried by alcohol and ether, when the layer of aluminate was scraped off with a knife, care being taken to avoid the separation of any of the unchanged metal. The aluminate was now further washed by the pump with cold water to insure the extraction of all free lime, and then with alcohol and ether.

## I. Dried over sulphuric acid some hours.

0.1854 gram substance gave 0.0609 gram  $\text{H}_2\text{O}$  and 0.0614 gram  $\text{Al}_2\text{O}_3$ .

	Calculated for $\text{Ca}_2\text{Al}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ .	Found.
$\text{H}_2\text{O}$	33.50	32.85
$\text{Al}_2\text{O}_3$	31.70	33.12
$\text{CaO}$ (diff.)	34.80	34.03

$\text{Al}_2\text{O}_3 : \text{CaO} : \text{H}_2\text{O} = 1 : 1.88 : 5.63$ .

## II. Dried over calcium chloride.

Analysis corrected for residue.<sup>1</sup>

0.2951 gram substance gave 0.1120 gram  $\text{H}_2\text{O}$ .

0.2183 gram substance gave 0.0652 gram  $\text{Al}_2\text{O}_3$

0.2183 gram contained 0.0038 gram insoluble residue = 1.74 percent; 0.2951 gram contains 0.0052 gram  $\text{Al}(\text{OH})_3$ , containing 0.0018 gram  $\text{H}_2\text{O}$ .

$\therefore$  0.2899 gram aluminate gave 0.1102 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{Ca}_2\text{Al}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$ .	Found.
$\text{H}_2\text{O}$	37.04	38.01
$\text{Al}_2\text{O}_3$	30.04	30.40
$\text{CaO}$ (diff.)	32.90	31.59

$\text{Al}_2\text{O}_3 : \text{CaO} : \text{H}_2\text{O} = 1 : 1.91 : 7.09$ .

*Calcium aluminate*,  $\text{Ca}_2\text{Al}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$ , is a dense, white, crystalline compound, having a pearly luster. Under the microscope transparent, hexagonal plates may sometimes be observed. It is quite difficultly soluble and only slowly acted upon by water.

By precipitation of hot lime-water by potassium aluminate a crystalline precipitate is obtained which, under the microscope, resembles  $\text{Sr}_3(\text{AlO}_3)_2 \cdot 6\text{H}_2\text{O}$ . Analysis indicated a similar composition.

0.2322 gram substance gave 0.0689 gram  $\text{H}_2\text{O}$ .

0.2152 gram substance gave 0.0546 gram  $\text{Al}_2\text{O}_3$ .

	Calculated for $\text{Ca}_3(\text{AlO}_3)_2 \cdot 6\text{H}_2\text{O}$ .	Found.
$\text{H}_2\text{O}$	28.56	29.68
$\text{Al}_2\text{O}_3$	27.02	25.33
$\text{CaO}$ (diff.)	44.43	44.99

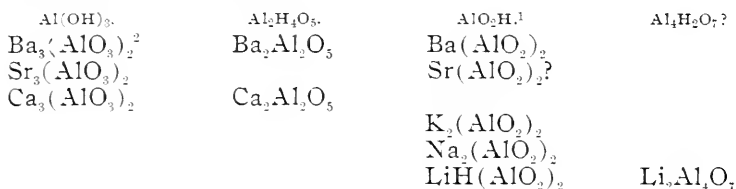
$\text{Al}_2\text{O}_3 : \text{CaO} : \text{H}_2\text{O} = 1 : 3.24 : 6.65$ .

<sup>1</sup> The aluminate dissolves in warm dilute hydrochloric acid, leaving a small quantity of a difficultly soluble white residue, probably crystalline aluminium hydroxide.

The preparation was washed with water, followed by 50 per cent alcohol, and finally by 95 per cent alcohol. It was dried over calcium chloride. It probably contained a little calcium carbonate.

### Summary.

1. The well-known aluminates may all, with one exception, be derived from the three hydroxides of aluminium. This exception, the anhydrous lithium aluminate, is not formed directly in the wet way.



2. The alkalis form aluminates belonging to the lowest type, *i. e.*, those into the composition of which the least base enters. The most soluble bases tried in our work form the least stable aluminates. They decompose with water, forming aluminium hydroxide which is crystalline or amorphous, according to the rapidity of the action. Lithium aluminate contains even less base than sodium and potassium aluminates. It is an acid salt, and being difficultly soluble, is quite stable.

The relative proportions of metal, water, and base, in the case of the alkalis, do not influence the type of salt formed, but do condition the decomposition of the salt.

3. The type of aluminate which the alkaline earths form, varies according to the conditions just mentioned. In the heat we obtained  $\text{Ba}_2\text{Al}_2\text{O}_5$ , while in the cold we could only obtain  $\text{Ba}(\text{AlO}_2)_2$ , even with the greatest excess of base. This was doubtless because only the portion in solution is active in the reaction, and that is greatly increased by the rise in temperature.

$\text{Sr}_3(\text{AlO}_3)_2$  is obtained where the strontia is in sufficient excess,  $\text{Sr}(\text{AlO}_2)_2(?)$  where the active mass is smaller.

<sup>1</sup> To this list should be added the aluminates of the spinel group, *viz.*,  $\text{Be}(\text{AlO}_2)_2$ ,  $\text{Mg}(\text{AlO}_2)_2$ , etc.

<sup>2</sup> Obtained by Beckmann: *J. prakt. Chem. (N. F.)*, **26**, 413.

Lime-water forms with metallic aluminium,  $\text{Ca}_2\text{Al}_2\text{O}_5$ . From hot lime-water,  $\text{Ca}_3(\text{AlO}_3)_2$  may be precipitated.

Taking the three alkaline earths together, we may say that the most soluble is least inclined to form aluminates of the highest type. As regards stability, it is unsafe to make comparisons because some are crystalline and some are amorphous, and the state of division of any solid conditions the rate of its chemical action. Thus the difference in the stability of  $\text{Sr}_3(\text{AlO}_3)_2$  and  $\text{Sr}(\text{AlO}_2)_2(?)$  is probably due to physical differences, for we should expect the former to be less stable than the latter, judging by its composition.

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## THE ACTION OF ALKALINE HYDROXIDES, OF WATER, AND OF HYDROGEN PEROXIDE UPON NITROGEN IODIDE.

BY F. D. CHATTAWAY AND K. J. P. ORTON.

Solutions of alkaline hydroxides rapidly decompose nitrogen iodide; the solid particles quickly disappear, bubbles of nitrogen are evolved even when light is excluded, and a pale yellow liquid is produced containing ammonia, together with hypiodite, iodate, and iodide of the base.

These facts were known to the chemists who first investigated the compound in Gay Lussac's laboratory. Gay Lussac himself, in his great paper on iodine,<sup>1</sup> states that when nitrogen iodide is placed in a solution of caustic potash it immediately disengages nitrogen and forms the same products as the element. These observations have been confirmed by all who have studied the reaction.

A partial explanation of it has recently been offered by Seliwanow, who regards it as a simple hydrolysis. He endeavored to establish his views experimentally, but was never able to reach more than approximate results.<sup>2</sup>

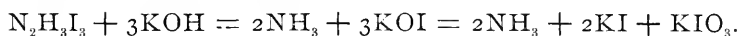
<sup>1</sup> Ann. Chim., 88, 304 (1813).

<sup>2</sup> Seliwanow (Ber. d. chem. Ges., 27, 102 (1894)), from his study of iodyl succinimide, recognized that compounds containing iodine attached to nitrogen should yield, on hydrolysis, hypiodous acid or hypiodites, or the products of their transformation. He treated nitrogen iodide with very dilute sulphuric or acetic acid and estimated the amount of iodine liberated and the amount of iodic acid remaining after



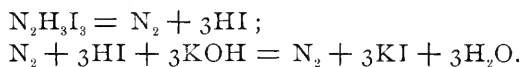
In continuation of our work upon pure nitrogen iodide we have investigated the action of alkalis and of water upon it, and have been able to prove that two reactions invariably occur simultaneously, the extent to which each takes place depending upon the conditions under which the decomposition is effected.

The chief action is one of hydrolysis, ammonia and an alkaline hypoiodite being produced. These hypoiodites, however, are unstable, and more or less rapidly change into iodide and iodate. The equations representing the action of potassium hydroxide, for example, are :



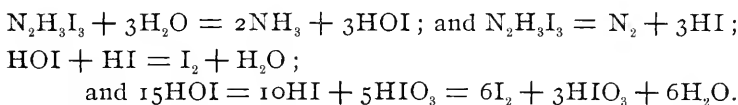
At the same time a portion of the nitrogen iodide always breaks down exactly as under the influence of light yielding nitrogen or hydrogen iodide, which latter then reacts with some of the alkaline hydroxide, forming an iodide.

For example, with potassium hydroxide, the reactions are :

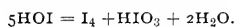


Solutions of ammonium hydroxide and of hydroxides of the alkaline earth metals act similarly.

Water also causes analogous decompositions, but in this case some of the hypoiodous acid formed in the hydrolysis reacts with the hydrogen iodide produced in the simple decomposition, liberating iodine, while any excess becomes itself transformed into iodine and iodic acid :



These reactions fully explain the production of iodine when this had been removed. The iodine and iodic acid should be formed in the proportion of 4 atoms of the former to 1 molecule of the latter :

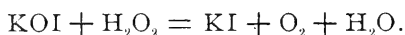


In eight recorded experiments he obtained numbers varying by about 25 per cent (from 4.6 to 3.6 atoms of iodine to 1 molecule of iodic acid). It was, however, impossible for him to obtain better results, since his explanation completely neglects the nitrogen evolved. Further, he did not know the composition of the material he was dealing with, and was thus unable to determine its purity. Indeed, he assumes that three compounds exist, and he gives equations representing the hydrolysis of each.

nitrogen iodide is warmed to 50°–60° C. with water, a method which Stas has employed to prepare pure iodine on a large scale.

The action of water on nitrogen iodide is rendered more rapid by the presence of basic oxides and of salts such as iodides and carbonates, which can combine or react with the hypiodous and hydriodic acids formed.<sup>1</sup>

Hydrogen peroxide dissolved in a solution of potassium hydroxide rapidly decomposes nitrogen iodide, ammonia, potassium iodide, and a trace of potassium iodate being produced, whilst oxygen, mixed with a little nitrogen, is evolved. The nitrogen iodide may be assumed to react with the potassium hydroxide as if it alone were present, being hydrolyzed to ammonia and potassium hypiodite, but at the same time breaking down partially into nitrogen and hydrogen iodide. A very small quantity of the hypiodite is transformed into iodide and iodate, but the greater part reacts with the hydrogen peroxide, liberating oxygen and being converted into iodide, thus :



If a solution of hydrogen peroxide be added to nitrogen iodide, no alkali being present, the water hydrolyzes the compound and similar reactions ensue, whilst iodine is set free by a further action of hydrogen peroxide on the hydrogen iodide remaining uncombined.

<sup>1</sup> In all reactions with nitrogen iodide where hydrolysis takes place, it is accompanied by a breaking down of the molecule into nitrogen and hydriodic acid, the amount of such decomposition altering with the conditions. A variable amount of hydriodic acid or iodine in excess of that corresponding with the decomposition of hypiodous acid and more approximately to that which would be needed by the action of a periodide is, therefore, always formed. In a paper by one of us (Chattaway : *Trans. Chem. Soc.*, 1896, 1572) attention was drawn to these variable results, and it was suggested that nitrogen iodide might be a periodide, and since, on analysis, the loss of nitrogen lowered the relative proportion of nitrogen to iodine, that it might have the formula  $\text{NH}_3\text{I}_2$ . This formula did account for the analytical results and grouped known facts better than any other could, assuming a single action in each case to take place. The composition of the pure substance has, however, now been established beyond doubt and found to correspond with the formula  $\text{N}_2\text{H}_3\text{I}_3$ , and it is further here shown that the variability and the excess of hydrogen iodide and iodine always noticed are due to secondary decompositions. The formula  $\text{NH}_3\text{I}_2$ , therefore, is incorrect, and with the above explanation of why it was suggested is unconditionally withdrawn.

*Action of Alkaline Hydroxides on Nitrogen Iodide.*

Nitrogen iodide, when placed in a strong solution of an alkaline hydroxide, disappears very rapidly, almost instantaneously if the liquid be hot; bubbles of pure nitrogen are evolved, ammonia is liberated, and a pale-yellow solution containing hypoiodite results. The hypoiodite soon becomes transformed into iodide and iodate, and the liquid loses its yellow color and its power of oxidizing arsenites. This change is complete after standing for twenty-four hours in the dark. The alkaline earth hydroxides, the slightly soluble basic oxides, and solutions of ammonia act similarly but more slowly.

The action of caustic potash, being typical, was chosen for careful study. A small quantity of pure crystalline nitrogen iodide was placed in a stoppered flask together with 14 cc. of a 36 per cent solution of potassium hydroxide, and allowed to stand in a perfectly dark, cool cellar at a uniform temperature for forty-eight hours. The nitrogen iodide was thus completely decomposed and all the hypoiodite converted into iodide and iodate.

The ammonia formed was first distilled off into standard acid and estimated. The solution was then made slightly acid with sulphuric acid and the liberated iodine titrated with sodium sulphite. This gives the iodate and consequently the hypoiodite originally produced. The total iodine in the product from the sulphite titration, and hence the quantity of nitrogen iodide used, was finally determined by silver nitrate.

Knowing the amounts of hypoiodite and ammonia produced, these can be compared and the hydrolysis quantitatively followed, while, since the total iodine contained in the nitrogen iodide is given by the silver nitrate titre, the percentage which undergoes decomposition into nitrogen and hydrogen iodide can be calculated.

$\frac{N}{10}$ $\text{NH}_3$ obtained by hydrolysis of portion of nitrogen iodide.	$\frac{N}{10} \left( \frac{\text{Na}_2\text{SO}_3}{2} \right)$ .	$\frac{N}{10}$ $\text{AgNO}_3$ = the total iodine in nitrogen iodide in cubic centimeters of a decinormal solution.	$\frac{1}{2} \left( \frac{N}{10} \frac{\text{Na}_2\text{SO}_3}{2} \right) = \frac{N}{10}$ KOI actually produced by hydrolysis of portion of nitrogen iodide.	Amount of potassium hypoiodite in cubic centimeters of $\frac{N}{10}$ KOI that should be produced, calculated from amount of ammonia obtained.	Ratio between $\text{NH}_3$ and KOI actually obtained.	Percentage of total nitrogen iodide used that decomposed into nitrogen and HI in the reaction.
cc.	cc.	cc.	cc.	cc.		
16.4	48.9	31.8	24.45	24.6	2.01 : 3	23.1
17.1	51.4	31.1	25.7	25.65	1.99 : 3	17.3
17.5	52.6	32.6	26.3	26.25	1.99 : 3	19.3
20.5	61.5	35.25	30.75	30.75	2 : 3	14.1

The agreement between the amount of hypoiodite estimated (column 4) and that calculated from the ammonia (column 5) is seen to be very close, although the second decomposition (column 7) has taken place to very different extents.

Experiments were next made in a similar manner, but instead of the hypoiodite being allowed to decompose into iodide and iodate before estimation, the yellow solution itself was analyzed, both the hypoiodite and iodate being determined. A quantity of crystalline nitrogen iodide was placed in from 15–20 cc. of a 28 per cent solution of potash and allowed to stand from thirty to sixty minutes in complete darkness. In this time the nitrogen iodide entirely decomposed, but a portion only of the hypoiodite was transformed into iodide and iodate. The hypoiodite was then estimated by arsenite, the iodate afterwards by sulphite, and finally the ammonia by distillation.

$\frac{N}{10} \left( \frac{Na_3AsO_3}{2} \right)$ required to react with potassium hypiodite formed	$\frac{N}{10} \left( \frac{Na_2SO_3}{2} \right)$ required to react with iodine liberated by the iodate.	$\frac{N}{10}$ $NH_3$ produced in distillation.	$\frac{1}{2} \left( \frac{N}{10} \frac{Na_3AsO_3}{2} \right) = \frac{N}{10}$ KOI actually present - a.	$\frac{1}{2} \left( \frac{N}{10} \frac{Na_2SO_3}{2} \right) = \frac{N}{10}$ KOI equivalent to iodate produced = b.	$\frac{N}{10}$ KOI actually produced by hydrolysis of portion of the nitrogen iodide = a + b.	$\frac{N}{10}$ KOI that should be obtained calculated from the amount of ammonia produced.	Ratio between $NH_3$ and KOI obtained.
cc.	cc.	cc.	cc.	cc.	cc.	cc.	
51.2	13.6	21.5	25.6	6.8	32.4	32.25	1.99 : 3
39.2	38.0	25.8	19.6	19	38.6	38.7	2 : 3
19.6	50.6	23.4	9.8	25.3	35.1	35.1	2 : 3

If nitrogen iodide be gradually added to a hot solution of caustic potash, light being entirely excluded, decomposition into nitrogen and hydriodic acid takes place to a very small extent only, almost all of the compound being hydrolyzed; ammonia is given off, and the conversion of the hypoiodite into iodide and iodate is rapid and complete. In order to investigate the action, about 0.5 gram of crystalline nitrogen iodide was added to 10 cc. of a 36 per cent solution of warm caustic potash, and the liquid rapidly heated to 100° and boiled for ten minutes. It was then cooled and acidified with sulphuric acid, after which the iodine liberated by the iodate was estimated by sodium sulphite. The total iodine present was finally determined by distillation with sulphuric acid and iron alum.

If the whole of the nitrogen iodide were hydrolyzed, the ratio of iodine as iodate to total iodine should be as 1 : 3, since



The ratio, however, is never quite reached, since some of the nitrogen iodide always decomposes into nitrogen and hydriodic acid, but the amount of this change, although variable, is not so large as when the substance is decomposed by cold potash. The conditions of the experiment affect the extent to which each change goes on.

In experiments 1-3, where the nitrogen iodide was added to a solution of potassium hydroxide heated to 60°, from 3-4

per cent only broke down into nitrogen and hydriodic acid, and in experiment 4, where it was added to a similar solution of potassium hydroxide already boiling 11.18 per cent, while, when allowed to decompose in potash of a similar strength at the ordinary temperature (see table, page 322), from 14-23 per cent so reacted.

Number of experiment.	$\frac{N}{10} \left( \frac{Na_2SO_3}{2} \right)$ required to react with iodine liberated by iodic acid produced.	$\frac{N}{10} \left( \frac{Na_2SO_3}{2} \right)$ required to react with iodine liberated by distillation with sulphuric acid and iron alum = total iodine as cubic centimeters of a decinormal solution.	$\frac{N}{10}$ I as $KIO_3$ in product = one-sixth of sulphite titre.	Ratio between iodine as iodate and total iodine in the product calculated as 1 : 3.	Percentage of nitrogen iodide decomposed into hydriodic acid and nitrogen in the experiment.
1	32.2	16.7	5.36	0.962 : 3	3.59
2	32.1	16.6	5.35	0.966 : 3	3.31
3	35.8	18.5	5.96	0.966 : 3	3.24
4	85.8	48.3	14.3	0.888 : 3	11.18

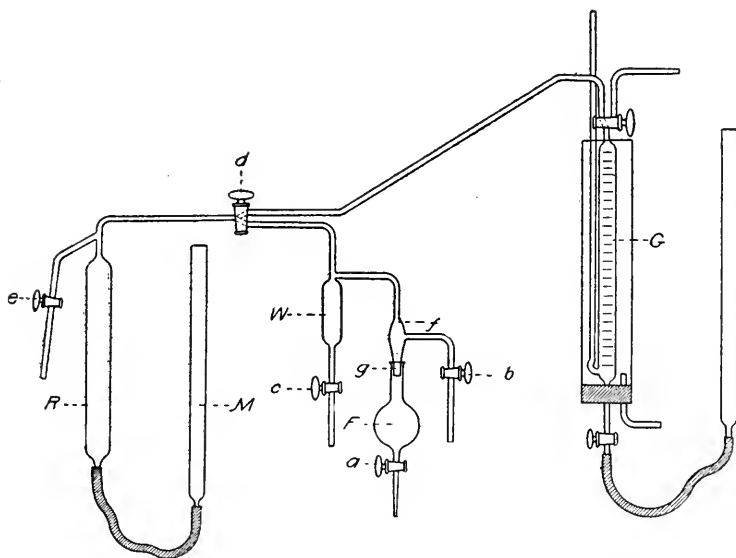
In order to complete the proof that two actions go on simultaneously when nitrogen iodide is decomposed by caustic potash, it is necessary to estimate the nitrogen evolved and to show that this corresponds with the amount calculated from the observed loss of ammonia.

In the following experiments, therefore, the decomposition of nitrogen iodide was effected in a specially constructed piece of apparatus which enabled small quantities of gas to be accurately measured while the liquid was not allowed to come into contact with mercury. Pure crystalline nitrogen iodide was used. It was decomposed by an excess of a 30 per cent solution of potassium hydroxide. The nitrogen evolved was measured and the alkaline liquid distilled, and the ammonia formed estimated. In the residue, after distillation, the iodate was determined by standard sodium sulphite after acidification with sulphuric acid, and finally the total iodine was estimated by distillation with sulphuric acid and iron alum.

Two estimations were made, and in each case the agreement between the actual (column 4) and calculated results

(columns 6 and 8) is so close as to put beyond question the correctness of the explanation given :

$\frac{N}{10} \text{ NH}_3$ cc.	$\frac{N}{10} \left( \frac{\text{Na}_2\text{SO}_3}{2} \right) = 2b$ cc.	$\frac{N}{10} \text{ I}$ contained in nitrogen iodide used = $a$ . cc.	Nitrogen evolved in cubic centi- meters at 0° and 760 mm. cc.	$\frac{N}{10} \text{ KOI}$ lost = $a - b$ . cc.	Nitrogen that should have been evolved calculated from total iodine and sulphite titre. cc.	$\frac{N}{10} \text{ NH}_3$ lost. cc.	Nitrogen that should have been evolved calculated from total iodine and ammonia obtained. cc.
10.1	30.2	18	2.12	2.9	2.161	1.9	2.128
8.4	25.2	15.1	1.82	2.5	1.866	1.67	1.87



Sodium hydroxide behaves towards nitrogen iodide in every respect as does potassium hydroxide. Ammonium hydroxide also acts similarly, with this exception, that, if nitrogen iodide be heated with a solution of ammonium hydroxide and the resulting solution rapidly cooled before the ammonium hypiodite, through transformation into iodate, falls below a

certain concentration, nitrogen iodide is reformed. The action is in this case reversible and obeys the laws of mass action. The effect of hydroxides of the alkaline earths is much the same except that it is slower, as weaker solutions have to be used.

*Action of Water on Nitrogen Iodide.*

Nitrogen iodide, when allowed to remain suspended in water at the ordinary temperature, light being excluded, slowly decomposes; bubbles of nitrogen are occasionally given off, free iodine is liberated, and ammonium iodide and iodate are formed. The action is very slow, some months being required before a gram or so completely disappears. After standing for some days under water the substance becomes very unstable, the slightest disturbance, even the rising of a bubble of gas, often being sufficient to cause an explosion. If nitrogen iodide be warmed with water to  $60^{\circ}$ – $65^{\circ}$ , the decomposition is rapid and explosions do not occur; free iodine separates in quantity, and ammonium iodate and iodide remain in the liquid. This latter mode of decomposition was employed by Stas<sup>1</sup> for preparing pure iodine.

No explanations of these reactions have been brought forward and we have consequently investigated them.

As in most other decompositions of nitrogen iodide, two reactions go on simultaneously, a simple hydrolysis of the substance resulting in the formation of ammonia and hypoiodous acid, and a breaking down of the compound into nitrogen and hydriodic acid. As the latter decomposition frequently takes place to a slightly greater extent than the former, the hydriodic acid is often produced in sufficient quantity to react with all the hypoiodous acid, so that no iodic acid is found. This, however, is not always the case, as the extent to which these two reactions take place varies with all the conditions of the experiment.

The results given below were obtained as follows: Small quantities of crystalline nitrogen iodide were placed in stoppered bottles of from 500–800 cc. capacity; these were then completely filled with water so as to exclude air, and left un-

<sup>1</sup> Chem. Propert, 137.



disturbed in a perfectly dark cellar for three months. At the end of that time the nitrogen iodide was found to have completely disappeared, a liquid colored brown by free iodine remaining. The free iodine in this was then estimated by sodium sulphite, the free hydriodic acid next by baryta, and finally the total iodine by silver nitrate. The ammonia present was then determined by distillation into standard acid after the addition of potash :

$N \frac{N_2SO_3}{10}$ cc.	$N \frac{Ba(OH)_2}{10}$ cc.	$N \frac{HI \text{ free in titrate } a.}{10}$ cc.	$N \frac{NH_3 \text{ obtained by distillation } b.}{10}$ cc.	Amount of $\frac{N}{10}$ $HOI$ actually produced in hydrolysis $= \frac{1}{2} \left( \frac{N_2SO_3}{2} \right) = c.$ cc.	Amount of $\frac{N}{10}$ $HOI$ that should be produced calculated from ammonia obtained by direct distillation. cc.	Amount of $\frac{N}{10}$ $HI$ produced in reaction obtained by subtracting amount of hypiodous acid formed from total iodine. cc.	Amount of $\frac{N}{10}$ $HI$ produced in reaction calculated from free iodine produced from amount of free $HI$ present after titration with sulphite given by baryta titre and from ammonia obtained in distillation $= (a+b)-c.$ cc.	Percentage of total nitrogen iodide hydrolyzed.	Percentage of total nitrogen iodide decomposed into nitrogen and hydriodic acid.
67.3	52.2	74.7	22.4	33.65	33.6	41.05	40.95	45.1	54.9
53	41.6	59.3	17.5	26.5	26.25	32.8	32.6	44.7	55.3
41.8	35.4	49.3	14	20.9	21	28.4	28.5	42.4	57.6
42.9	35.1	49.4	14.3	21.45	21.45	27.95	27.95	43.5	56.5

The agreement between the amounts of hypiodous acid actually formed and those calculated from the ammonia produced, and between the amounts of hydriodic acid formed in the reaction calculated from quite different titration numbers proves beyond question that the explanation of the reaction given above is correct.

Nitrogen iodide is decomposed much more readily by a solution of potassium iodide than by pure water, only a few hours being required.

If light be excluded, no nitrogen is evolved, and hydrolysis of the nitrogen iodide only appears to take place, the potassium iodide reacting with the hypiodous acid and holding the liberated iodine in solution.

In the following experiments nitrogen iodide was treated with an excess of a decinormal solution of potassium iodide, light being completely excluded. After the disappearance of the solid particles, which generally happened in from eight to twelve hours, the resulting liquid was analyzed as follows: It was considerably diluted and the free iodine titrated with sodium sulphite; the free hydriodic acid then present was estimated by baryta, and finally the whole was distilled with potash and the ammonia evolved estimated by standard acid.

The amount of hypiodous acid corresponding to the free iodine is found, as in all other cases, to agree with that calculated from the ammonia produced, while the fact that no decomposition of the substance into nitrogen and hydriodic acid accompanies this is proved by the circumstance that the amount of the ammonia actually obtained is exactly that which should be produced, calculated from the sulphite and baryta titres.

$\frac{N}{10} \left( \frac{Na_2SO_3}{2} \right)$ cc.	$\frac{N}{10} \left( \frac{Ba(OH)_2}{2} \right) = \text{free } \frac{N}{10} HI$ cc.	$\frac{1}{2} \left( \frac{N}{10} \frac{Na_2SO_3}{2} \right) - \frac{N}{10} \left( \frac{Ba(OH)_2}{2} \right) = \frac{N}{10} NH_3 \text{ that should be produced, assuming that hydrolysis only takes place.}$ cc.	$\frac{N}{10} NH_3 \text{ actually obtained by distillation with potash.}$ cc.	$\frac{N}{10} HIO \text{ produced calculated from ammonia actually obtained.}$ cc.	$\frac{N}{10} HIO \text{ formed } = \frac{1}{2} \frac{N}{10} \left( \frac{Na_2SO_3}{2} \right)$ cc.
45.5	7.5	15.25	15.1	22.65	22.75
55.8	9.3	18.6	18.5	27.75	27.9
48.7	8.1	16.25	16.2	24.3	24.35

The presence of slightly soluble oxides, as, for example, those of magnesium and lead, somewhat accelerates the action of water upon nitrogen iodide, and the acids formed react with them to form iodides and iodates of the metals.

#### *Action of Hydrogen Peroxide upon Nitrogen Iodide.*

A solution of hydrogen peroxide alone or in presence of caustic potash, when brought into contact with nitrogen iodide, decomposes it with great rapidity, and oxygen mixed with small quantities of nitrogen is evolved. If hydrogen per-

oxide alone be used, iodine is liberated and ammonium iodide produced, while, if caustic potash be employed, free ammonia, potassium iodide, and a very small quantity of iodate are formed. A quantity of pure crystalline nitrogen iodide was treated, in the apparatus used in studying the action of potassium hydroxide, with a solution of hydrogen peroxide, and all the products estimated. The gas evolved was analyzed and found to consist only of oxygen mixed with a small proportion of nitrogen. In the liquid product of the reaction, which contained ammonium iodide and free iodine, the ammonia was estimated by distillation into standard acid, and the iodine, after conversion into hydriodic acid by sodium sulphite, was titrated with silver nitrate.

From the amount of ammonia formed, the quantity of nitrogen iodide hydrolyzed can be calculated, and consequently the volume of oxygen that should be obtained by the reaction of the hypoiodite with the hydrogen peroxide. The silver nitrate titre gives the total iodine in the nitrogen iodide used, and the ammonia, the amount hydrolyzed; the quantity, therefore, which has decomposed into nitrogen and hydriodic acid in the reaction, and the volume of nitrogen that should be evolved can be calculated.

The following table gives a comparison of the amounts of oxygen and nitrogen thus calculated with those actually obtained. The numbers given are a mean of two experiments :

$\frac{N}{cc.} \frac{AgNO_3}{10} = \frac{N}{10} \frac{I}{cc.}$ in the nitrogen iodide used.	$\frac{N}{cc.} \frac{NH_3}{10}$ obtained by distillation.	Amount of oxygen that should be evolved calculated from amount of nitrogen iodide hydrolyzed.	Amount of nitrogen that should be evolved calculated from amount of nitrogen iodide that decomposed into nitrogen and hydriodic acid.	Total amount of gas evolved at 0° c. and 760 mm.	Total oxygen actually obtained c. in experiment.	Total nitrogen actually obtained c. in experiment.
18.00	10.4	34.83	1.79	37.48	36.16	1.32

The results obtained are sufficiently close to show that the explanation given is the correct one, but, as might be expected, the nitrogen is slightly too low, owing to a portion be-

ing dissolved in the liquid employed; while the oxygen is somewhat too high, this being due to the fact that hydrogen peroxide itself, under the circumstances of the experiment, slowly gives off oxygen, an action which cannot be prevented or estimated.

In the next experiment the hydrogen peroxide was mixed with caustic potash to prevent the deposition in the apparatus of free iodine which is very difficult to remove completely for purposes of estimation.

Here a portion of the hypoiodite escapes the action of the hydrogen peroxide and becomes converted into iodate. When the ammonia had been distilled off, this was estimated by sodium sulphite after acidification with sulphuric acid. It was allowed for in the calculation by subtracting the amount of hypoiodite equivalent to it from the total amount produced in the hydrolysis. As before, a comparison is made in the table between the amounts of oxygen and nitrogen actually measured and those which should be evolved, calculated from the amounts of nitrogen iodide hydrolyzed and decomposed into nitrogen and hydriodic acid, respectively:

$\frac{N}{10} \text{ AgNO}_3$ cc.	$\frac{N}{10} \text{ NH}_3$ cc.	$\frac{N}{10} \left( \frac{\text{Na}_2\text{SO}_3}{2} \right)$ required to reduce iodate. cc.	Amount of oxygen that should be evolved. cc.	Amount of nitrogen that should be evolved. cc.	Total amount of gas evolved at 0° and 760 mm. cc.	Total oxygen actually obtained. cc.	Total nitrogen actually obtained. cc.
25.6	14.8	11.6	36.34	2.51	39.89	38.05	1.84

Again, the nitrogen is slightly too low, a little being lost by solution in the liquid, while the oxygen is somewhat high, the excess being produced as before by the spontaneous decomposition of nitrogen peroxide during the experiment.

In the calculations oxygen is taken as 15.84, the weight of 1 cc. of nitrogen as 0.0012507 gram, and that of 1 cc. of oxygen as 0.0014293 gram.

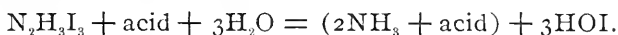
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## THE ACTION OF ACIDS UPON NITROGEN IODIDE.

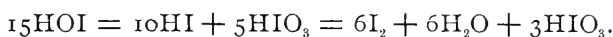
BY F. D. CHATTAWAY AND H. P. STEVENS.

Most chemists who have investigated nitrogen iodide have recorded observations on its behavior towards a few of the commoner acids, so that the ultimate products of such treatment are tolerably well known. The reactions, however, have never been carefully studied nor has any explanation of them been brought forward.

Dilute acids, when added to nitrogen iodide suspended in water, first induce hydrolysis of the compound, and hypoiodous acid is liberated, together with ammonia, which combines with the acid added :

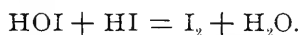


The further action depends upon the nature of the acid used. If acids be employed such as sulphuric, phosphoric, boric, or acetic, upon which hypoiodous acid has no effect, a rapid change into hydriodic and iodic acids occurs, the former being immediately oxidized by a portion of the latter and iodine liberated :

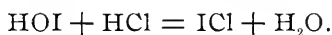


If, however, interaction between the acid used and hypoiodous acid is possible, this takes place, and the nature of the final products depends upon the acid employed.

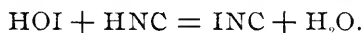
With hydriodic acid, for example, iodine is liberated according to the equation :



With hydrochloric acid, iodine monochloride is produced :



While with hydrocyanic acid cyanogen iodide is formed :



In addition to this main action, it is found that, when any acid except hydriodic or hydrocyanic is added to nitrogen iodide, light being excluded, a variable amount, depending on the strength of the acid and all other conditions, decom-

poses exactly as it does under the influence of light, yielding nitrogen and hydriodic acid; this hydriodic acid then reacts with some of the hypiodous acid formed in the hydrolysis and liberates iodine.

*General Behavior of Nitrogen Iodide towards Acids.*

Most acids, if at all concentrated, act very violently upon nitrogen iodide and generally cause explosion. A strong solution of sulphurous acid, even when poured over dry nitrogen iodide, causes it to deteriorate. If, however, the nitrogen iodide be suspended in water, and a solution of acid of about decinormal strength added, rapid, but quiet, decomposition ensues, bubbles of nitrogen generally rise from the decomposing particles which float to the surface, and when the action is over free iodine is, as a rule, found in the liquid.

The actions of hydriodic acid and of hydrocyanic acid are first considered, as these are not complicated by any simultaneous decomposition into nitrogen and hydriodic acid.

*Action of Hydriodic Acid upon Nitrogen Iodide.*

When a solution of hydriodic acid is added to water containing nitrogen iodide in suspension, the nitrogen iodide is at once decomposed, ammonium iodide is formed, and iodine liberated, no nitrogen being evolved if light be entirely excluded.

In the experiments made to determine the course of the reaction, small quantities of crystalline nitrogen iodide were completely decomposed by the addition of known amounts of a decinormal solution of hydriodic acid. The iodine set free was then estimated by a standard solution of neutral sodium sulphite, whereby it was converted into free hydriodic acid. The amount of free acid in the solution was next estimated by neutralizing the liquid with standard baryta, and finally the total hydriodic acid was determined by standard silver nitrate.

Knowing the amount of hydriodic acid present from the silver titre, if that added to decompose the compound be subtracted, the quantity produced from the nitrogen iodide is obtained. This is found to contain iodine equivalent to half the iodine liberated in the free state; the other half must, therefore,

have been obtained from the hydriodic acid added. Thus all the iodine contained in the nitrogen iodide behaves as if it were first liberated as hypoiodous acid. —

Also, knowing the total quantity of hydriodic acid present from the silver titre and the amount free from the baryta titre, the ammonia produced which neutralizes the remainder can be calculated. This can also be determined by distilling the final product with caustic potash. Both methods have been adopted. In every case the amount is found to equal that calculated from the free hydriodic acid produced, showing that the nitrogen iodide entirely hydrolyzes into hypoiodous acid and ammonia.

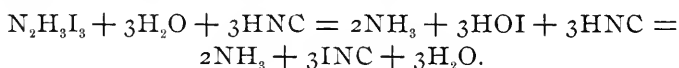
$\frac{N}{10}$ HI added to decompose the nitrogen iodide = <i>a</i> .	$\frac{N}{10} \left( \frac{Na_2SO_4}{2} \right)$ = total amount of iodine liberated as cubic centimeters of $\frac{N}{10}$ I.	$\frac{N}{10} \frac{Ba(OH)_2}{2}$ = amount of $\frac{N}{10}$ HI free.	$\frac{N}{10} AgNO_3$ total amount of $\frac{N}{10}$ HI present after titration with sulphite = <i>b</i> .	$b - a = \frac{N}{10}$ HI obtained from nitrogen iodide = $\frac{N}{10}$ I contained in nitrogen iodide.	Half the iodine liberated in free state as $\frac{N}{10}$ I.	$\frac{N}{10} NH_3$ produced = total amount of $\frac{N}{10}$ HI — amount of $\frac{N}{10}$ HI free.	$\frac{N}{10} NH_3$ produced estimated by distillation.	$\frac{N}{10} NH_3$ that should be produced calculated from amount of HI yielded by nitrogen iodide.
cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.
31.8	60.1	41.9	61.9	30.1	30.05	20.	...	20.06
53.0	83.8	67.0	94.9	41.9	41.9	27.9	...	27.93
31.7	40.5	...	52.0	20.3	20.25	...	13.5	13.53
31.8	46.8	...	55.2	23.4	23.4	...	15.6	15.6

### *Action of Hydrocyanic Acid upon Nitrogen Iodide.*

Dilute hydrocyanic acid rapidly decomposes nitrogen iodide, and a colorless solution results, containing, if light be entirely excluded, only cyanogen iodide and ammonia. On shaking this solution with ether, the cyanogen iodide is extracted, and crystallizes in white needles on allowing the solvent to evaporate, while the ammonia can be obtained by distilling the residue with potash. Estimations have been made of the amounts of nitrogen iodide required to react with known volumes of a standard solution of hydrocyanic acid, the quantity of the former being determined from the ammonia produced. If the solution of hydrocyanic acid be added to the nitrogen iodide,

it is difficult to decompose the last few particles without adding an excess. In the experiments, therefore, it was added to a quantity of nitrogen iodide slightly in excess of the amount required to react with it; the liquid was vigorously shaken for some minutes and the unchanged solid filtered off.<sup>1</sup> The filtrate was then very slightly acidified by sulphuric acid and the cyanogen iodide driven off by rapidly boiling. A little silver nitrate solution was added at the end of the operation to show that the expulsion was complete.

No weighable amount of silver iodide was ever formed, showing that the cyanogen iodide could be expelled thus without hydrolysis, and that no hydriodic acid was produced in the previous reaction. The residue was then made alkaline with caustic potash, and the ammonia distilled off into standard acid. The amount of nitrogen iodide which reacted with the known amount of hydrocyanic acid used can be calculated from this ammonia. In the following results this is shown to be in accord with the equation:



$\frac{\text{N}}{10}$ HNC which reacted with nitrogen iodide used.	$\frac{\text{N}}{10}$ NH <sub>3</sub> produced in distillation.	$\frac{\text{N}}{10}$ I contained in nitrogen iodide used calculated from ammonia produced = $\frac{\text{N}}{10}$ HNC required by above equation.
cc.	cc.	cc.
19.7	13.4	20.1
21.7	14.7	22.05

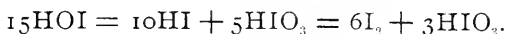
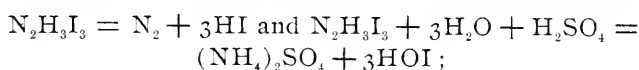
#### *Action of Sulphuric Acid upon Nitrogen Iodide.*

Dilute sulphuric acid added in excess to nitrogen iodide suspended in water immediately liberates iodine, while bubbles of nitrogen gas are given off. If the resulting liquid be boiled so as to expel all the free iodine, it is found to contain, besides excess of sulphuric acid, ammonium sulphate and iodic acid. Two reactions here go on simultaneously, a small percentage of the nitrogen iodide breaks up into hydriodic acid and free nitrogen, but the greater part suffers hydrolysis under the influence of the dilute sulphuric acid, producing

<sup>1</sup> As a precaution, this nitrogen iodide filtered off was analyzed and found to be unchanged in composition.



ammonium sulphate and hypiodous acid;<sup>1</sup> a portion of the latter oxidizes the hydriodic acid already formed, liberating iodine, while the remainder undergoes transformation into hydriodic and iodic acids, yielding finally iodine and iodic acid, since the latter, if light be excluded, is always in excess. The following equations represent the changes taking place:



The nitrogen and hydriodic acid formed in the direct decomposition do not prevent an estimation of the ammonia and hypiodous acid produced in the hydrolysis. Such an estimation shows that these compounds are formed in the proportion required by the second equation.

In the experiments an unknown quantity of pure nitrogen iodide was suspended in water and treated with an excess of decinormal sulphuric acid. After standing for about fifteen minutes to complete the decomposition, light being entirely excluded, decinormal sodium sulphite was added until the last trace of free iodine disappeared.

The total hypiodous acid produced in the hydrolysis is measured by half the sulphite titre, since the sulphite measures the iodine liberated, and this is the same whether liberated previously to or during the actual titration by either the hypiodous acid or the iodic acid yielded by it. The solution was next neutralized by caustic potash, and the total iodide estimated by silver nitrate, and finally excess of potash was added and the ammonia distilled off into standard acid.

From the sulphite titre, the amount of ammonia that should be liberated in the hydrolysis, assuming it to take place according to the above reaction, can be calculated and compared with the amount actually obtained. The agreement in every case was found to be within the limits of experimental error. From the sulphite titre also the amount of iodine contained in

<sup>1</sup> The evidence for the formation of hypiodous acid in this and similar reactions is largely indirect. If the acid product, however, be distilled immediately after the escape of the iodine, a very small quantity of a volatile compound, capable of liberating iodine from potassium iodide, passes over. This is probably a trace of hypiodous acid which has not passed over with the iodine and has escaped transformation.

the portion of the nitrogen iodide hydrolyzed is obtained, while the iodine contained in the whole of the nitrogen iodide is given by the silver titre. The percentages undergoing hydrolysis and decomposition into nitrogen and hydriodic acid, respectively, can therefore be calculated :

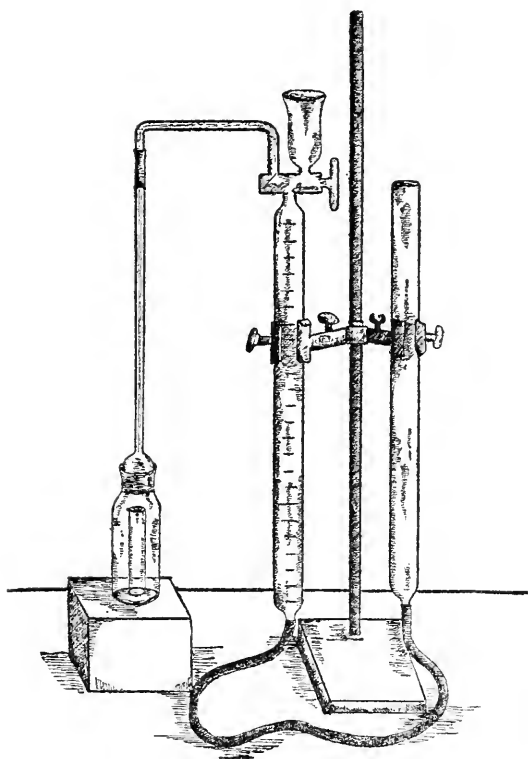
$\frac{N}{10} \left( \frac{Na_2SO_3}{2} \right)$ = free iodine + iodine liberated by iodic acid during titration. cc.	$\frac{N}{10} AgNO_3 = \frac{N}{10} I$ present in whole of nitrogen iodide used = <i>a</i> . cc.	$\frac{1}{2} \left( \frac{N}{10} \frac{Na_2SO_3}{2} \right) = \frac{N}{10} HOI$ formed by hydrolysis of a portion of the nitrogen iodide = <i>b</i> . cc.	Amount of $\frac{N}{10} NH_3$ that should be produced in hydrolysis calcu- lated from amount of hypiodous acid produced. cc.	$\frac{N}{10} NH_3$ actually obtained in dis- tillation. cc.	$a - b = \frac{N}{10} HI$ obtained by de- composition of a portion of the nitrogen iodide into nitrogen and hydriodic acid. cc.	Percentage of nitrogen iodide used which decomposed into nitrogen and hydriodic acid.
56.7	32.8	28.35	18.9	18.9	4.45	13.5
41.8	23.9	20.9	13.9	13.9	3.0	12.5
27.2	16.2	13.6	9.06	9.1	2.6	16.0

These experiments and the fact that iodic acid is always produced prove that the greater part of the nitrogen iodide hydrolyzes under the influence of the acid.

To complete the proof it is necessary to show that the amount of nitrogen evolved corresponds with the remainder. The apparatus shown in the figure was employed :

It consisted of a bottle of about 100 cc. capacity, inside which a small tube was sealed. The bottle was ground on to a long glass tube of very narrow bore, which was attached to a measuring burette. In the experiments a convenient quantity of moist crystalline nitrogen iodide was placed in the inner, and about 40 cc. of decinormal sulphuric acid in the outer, compartment. The apparatus was then connected with the measuring burette and allowed to stand for twenty minutes in a deep cellar without windows, where the temperature did not vary 0°.1 in twenty-four hours. The acid was then run on to the nitrogen iodide. After two hours, when all action had entirely ceased, the evolved gas was measured,<sup>1</sup> and the other products of the decomposition estimated. The liquid was first titrated with sodium sulphite, then the ammonia was dis-

<sup>1</sup> The gas was shown to be pure nitrogen in a separate experiment.



tilled off after rendering alkaline with potash, and finally the total iodine present was determined by distillation with sulphuric acid and iron alum :

$\frac{N}{10} \left( \frac{Na_2SO_3}{2} \right) = a.$						
cc.						
35.7						
35.4						
$\frac{a}{2} = \frac{N}{10}$ HOI produced.						
cc.						
17.85						
17.7						
$\frac{N}{10}$ I obtained from nitrogen iodide, from which amount of latter used can be calculated.						
cc.						
20.7						
21.4						
$\frac{N}{10}$ NH <sub>3</sub> produced in reaction.						
cc.						
12.0						
11.6						
Nitrogen evolved in cubic centimeters at 0° and 760 mm.						
cc.						
2.11						
2.91						
Nitrogen that should have been evolved calculated from amount of nitrogen iodide used and amount of hypoiodite formed.						
cc.						
2.12						
2.76						
Nitrogen that should have been evolved calculated from amount of nitrogen iodide used and amount of ammonia produced.						
cc.						
2.01						
2.98						

The close agreement between the amounts of nitrogen actually measured and those calculated, both from the amount of hypoiodite and from the amount of ammonia produced, show that the hypothesis of two reactions taking place simultaneously is completely justified.

*Action of Phosphoric, Boric, and Acetic Acids upon  
Nitrogen Iodide.*

These three acids act upon nitrogen iodide much as dilute sulphuric acid does. Two reactions go on simultaneously; a certain proportion, varying with the acid, breaks up into hydriodic acid and nitrogen, while the remainder is hydrolyzed, yielding an ammonium salt and hypoiodous acid, or the products of its transformation. The experiments were carried out much as with sulphuric acid.

With boric acid decomposition was much slower and the percentage hydrolyzed much smaller than with the stronger acids; the same, to a less degree, is true of acetic acid.

During the decomposition of nitrogen iodide by boric acid, small quantities frequently explode spontaneously under the surface of the liquid. As a rule, these explosions are not sufficiently violent to break the flask or splash the contents, and analyses of the products after such explosions show that in them the compound simply breaks down suddenly into nitrogen and hydriodic acid. The ammonia and hypoiodous acid are found to be produced in the same relative quantities as when no explosion occurs, the only difference being that a smaller percentage is hydrolyzed.

Decinormal solutions of phosphoric and acetic acids were used, while, as a decinormal solution of boric acid  $\frac{\text{H}_3\text{BO}_3}{3 \times 10}$  decomposes nitrogen iodide rather slowly, a stronger solution containing 5 grams to the liter was used.

In the experiments recorded in the following table, numbers 1 and 2 were made with phosphoric acid, 3 and 4 with boric, and 5 and 6 with acetic acid :

Number of experiment.	$\frac{N}{10} \left( \frac{Na_2SO_3}{2} \right) =$ free iodine + iodine liberated by iodic acid during titration.	$\frac{N}{10} AgNO_3 = \frac{N}{10} I$ present in whole of nitrogen iodide used = <i>a</i> .	$\frac{1}{2} \left( \frac{N}{10} \frac{Na_2SO_3}{2} \right) = \frac{N}{10} HOI$ formed by hydrolysis of portion of the nitrogen iodide = <i>b</i> .	Amount of $\frac{N}{10} NH_3$ that should be produced in hydrolysis calculated from amount of hypiodous acid produced.	$\frac{N}{10} NH_3$ actually obtained in distillation.	$a - b = \frac{N}{10} HI$ obtained by decomposition of a portion of the nitrogen iodide into nitrogen and hydriodic acid.	Percentage of nitrogen iodide used which decomposed into nitrogen and hydriodic acid.
1	42.1	24.4	21.05	14.03	13.9	3.35	13.7
2	40.6	23.6	20.3	13.53	13.5	3.3	13.9
3	44.1	36.4	22.05	14.7	14.6	14.35	39.4
4	36.2	30.4	18.1	12.06	12.0	12.3	40.4
5	36.7	23.3	18.35	12.23	12.2	4.95	21.2
6	40.6	26.3	20.3	13.53	13.6	6.0	22.8

A solution of oxalic acid also decomposes nitrogen iodide just as acetic acid does, the two usual reactions taking place simultaneously, but, as hypiodous acid readily oxidizes oxalic acid, carbon dioxide is also produced.

#### *Action of Hydrochloric Acid upon Nitrogen Iodide.*

The addition of strong hydrochloric acid to dry nitrogen iodide causes an immediate explosion. The action of dilute hydrochloric acid upon the moist substance is less violent and can be investigated. A normal solution of hydrochloric acid, when added in excess to nitrogen iodide suspended in water, rapidly decomposes it, bubbles of nitrogen are given off, and a red-brown solution containing much iodine monochloride and a small quantity of free iodine results. If this solution be repeatedly extracted with ether, the colorless residual liquid is found to contain ammonium chloride, free hydrochloric acid, and a very small quantity of iodic acid.

The fact that iodic acid is found leads to the conclusion that the first action of hydrochloric, like that of other acids, is to induce hydrolysis. Most of the hypiodous acid thus produced then interacts with hydrochloric acid, forming water and iodine monochloride, but a portion escapes this action and becomes transformed into iodine and iodic acid. This is pos-

sible, since the hydrochloric acid is added to the nitrogen iodide, and therefore, at first, is not present in excess, and since iodic acid, when formed, is not at the ordinary temperature able to react with hydrochloric acid. At the same time, as in other cases, a portion of the nitrogen iodide breaks down into nitrogen and hydriodic acid, the latter of which reacts either with the hypiodous acid or the iodine monochloride to form a further and much larger quantity of free iodine. The iodine, iodine monochloride, and iodic acid are together equivalent to the hypiodous acid produced, and on estimating these by sulphite, and the ammonia formed by distillation with potash, it is found that the ammonia calculated from the sulphite titre corresponds with that actually obtained, proving that all are formed from nitrogen iodide by hydrolysis.

In presence of the excess of hydrochloric acid, it is not easy, after titration with sulphite, to estimate directly the total hydriodic acid, but this can be obtained, and consequently the total amount of nitrogen iodide used, by titrating with silver nitrate and subtracting from the titre the amount of hydrochloric acid originally added. The percentage decomposing into nitrogen and hydriodic acid can thus be calculated.

$\frac{N}{10} \left( \frac{Na_2SO_3}{2} \right) =$ free iodine + iodine liberated by ICl and $HIO_3$ during titration. cc.	$\frac{N}{10}$ I contained in nitrogen iodide used = $a$ . cc.	$\frac{1}{2} \left( \frac{N}{10} \frac{Na_2SO_3}{2} \right) = \frac{N}{10}$ HOI formed by hydrolysis of a por- tion of the nitrogen iodide = $b$ . cc.	Amount of $\frac{N}{10}$ $NH_3$ that should be produced in hydrolysis calcu- lated from amount of HOI pro- duced. cc.	$\frac{N}{10}$ $NH_3$ actually obtained in distillation. cc.	$a - b = \frac{N}{10}$ HI obtained by de- composition of a portion of the nitrogen iodide into nitrogen and hydriodic acid. cc.	Percentage of nitrogen iodide used which decomposed into ni- trogen and hydriodic acid.
68.4	37.8	34.2	22.8	22.7	3.6	9.52
66.2	38.2	33.1	22.06	22.1	5.1	13.37

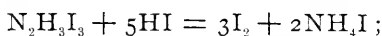
If, instead of adding hydrochloric acid to the moist compound, pure amorphous nitrogen iodide suspended in water be very gradually added to a large excess of decinormal hydrochloric acid, the whole is hydrolyzed, no bubbles of nitrogen are evolved, and no iodine is set free, but a clear orange-

colored solution results, containing, besides excess of hydrochloric acid, only iodine monochloride and ammonium chloride. The iodine monochloride can be completely extracted by repeatedly shaking the product with ether and, after such extraction, the resulting liquid is colorless, and contains no trace of iodic acid.

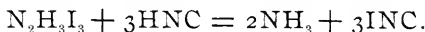
The following experiments show that the iodine monochloride then corresponds with the ammonia formed :

$\frac{N}{10}$ $\text{NH}_3$ obtained by distillation with KOH. cc.	Amount of $\frac{N}{10}$ $\text{ICl}$ that should be produced from $\text{HOI}$ formed by hydrolysis of nitrogen iodide yielding the quantity of ammonia obtained. cc.	Amount of $\frac{N}{10}$ $\text{ICl}$ actually estimated by sodium sulphite. cc.
18.5	27.75	27.85
21.3	31.95	31.9

In conclusion, it may be mentioned that the results obtained with hydriodic and hydrocyanic acids and those with hydrochloric acid, where iodine monochloride only is formed, can equally well be represented as direct interaction between nitrogen iodide and the acid by equations, such as



and



The fact, however, that iodic acid is produced when strong hydrochloric is added to nitrogen iodide, and that with all acids incapable of reacting with hypoiodous acid, hydrolysis undoubtedly occurs, renders it more probable that here too the same happens, and that the iodine, cyanogen iodide, and iodine monochloride are subsequently formed. In any case, by the aid of such an hypothesis, the reaction can be conveniently grouped and followed.

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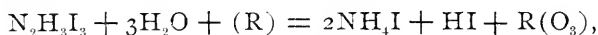
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# THE FORMATION AND CONSTITUTION OF NITROGEN IODIDE.

By F. D. CHATTAWAY AND K. J. P. ORTON.

In the preceding papers it has been shown that nitrogen iodide is a perfectly definite chemical compound, obtainable in a crystalline form. All the methods of preparation yet known yield only a single substance, the composition of which is represented by the formula  $N_2H_3I_3$ . With this knowledge of its composition we have been able to follow quantitatively its reactions.

Its oxidizing action may be represented by the equation



where R stands for any reducing agent. The iodine present in nitrogen iodide therefore exerts twice its normal oxidizing action.

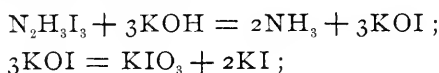
Under all circumstances nitrogen iodide shows a tendency to break down into nitrogen and hydriodic acid, thus :



This decomposition takes place with great rapidity under the influence of light.

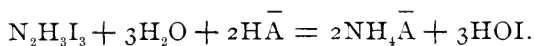
There is but little doubt that, in the explosion of nitrogen iodide, a similar decomposition takes place. When treated with acids nitrogen iodide frequently explodes, and we have shown that, under these circumstances, where there is no loss of the substances formed, a much greater amount of the iodide decomposes into nitrogen and hydriodic acid than occurs in the absence of explosion.

In the ready decomposition of nitrogen iodide by acids and alkalis, two separate reactions take place concomitantly, hydrolysis and a decomposition into nitrogen and hydriodic acid. Thus, with alkalis :



with acids :





The final products are determined by the nature of the acid. Hydrochloric and hydrocyanic acids react with the hypoiodous acid to form iodine monochloride and cyanogen iodide; hydriodic acid to liberate iodine. With other acids the final products are the ammonium salt of the acid, iodic acid, and iodine.

These reactions leave no doubt that in nitrogen iodide neither iodine nor hydriodic acid is present in loose molecular combination, such as occurs in periodides or acid iodides. Each atom of iodine is monovalent, and directly linked with nitrogen.

From a study of the action of iodine on potash, soda, and ammonia, Schönbein concluded that in all cases the initial products were iodide and a hypoiodite, and suggested that nitrogen iodide was formed by a decomposition of ammonium hypoiodite and not by direct substitution. This view was endorsed by Selewanow, who attempted to show qualitatively<sup>1</sup> that a hypoiodite remained in the ammoniacal solution after precipitation of nitrogen iodide.

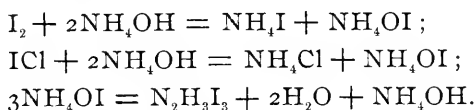
To elucidate this point fully, we have studied quantitatively the actions of iodine and iodine monochloride on ammonia, the oxidation of arsenite being used as a means of estimating hypoiodite, the formation of which always accompanies the formation of nitrogen iodide.

In the case of free iodine exactly half, and in the case of iodine monochloride the whole of the iodine present appears as nitrogen iodide and hypoiodite, or as ammonium iodide and iodate, the transformation products of the latter. Further, we find that addition of ammonia to a solution of an alkaline hypoiodite is followed directly by the separation of nitrogen iodide.

When an alkaline solution of potassium hypoiodite of known strength is used, and the hypoiodite estimated in the filtrate from the precipitated nitrogen iodide, the iodine as hypoiodite in the filtrate is found to be less than the iodine as hypoiodite originally present, by an amount which equals the

<sup>1</sup> He used, as a test for hypoiodite, the liberation of iodine on addition of potassium iodide.

iodine as nitrogen iodide. The latter is, therefore, formed at the expense of the hypoiodite, and the following equations must represent the action of iodine and iodine monochloride on solutions of ammonia :



The reaction represented by the last equation is never complete, a certain small amount of hypoiodite remaining in the solution and becoming transformed into iodate and iodide.

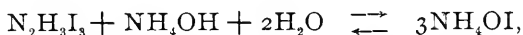
Thus, though in the action of iodine on ammonia only half the iodine originally becomes iodide, this quantity increases somewhat at the expense of the hypoiodite.

Exact experiments further show that treatment of nitrogen iodide by a solution of ammonia leads to the formation of ammonium hypoiodite.

The concentration of hypoiodite reached is always very small,<sup>1</sup> and attains its maximum value in the course of half an hour ; it is constant for a given concentration of ammonia and a given temperature, but increases with the increase of either.

The simplest explanation<sup>2</sup> of all the observed facts appears to be that ammonium hypoiodite is very unstable, and when formed immediately decomposes into nitrogen iodide and ammonia. The action, however, is a reversible one, and consequently a small amount of ammonium hypoiodite remains unaltered in the mother-liquor, while a corresponding amount is formed in a solution of ammonia placed in contact with nitrogen iodide.

If we have a reversible action represented by



<sup>1</sup> The maximum concentration, we have observed, was such that 100 cc. of the ammoniacal solution oxidized 3.3 cc. of  $\frac{\text{N}}{10}$  arsenite.

<sup>2</sup> It is impossible to say definitely whether the substance dissolved in the ammoniacal supernatant liquor is nitrogen iodide itself or the product of its hydrolysis, ammonium hypoiodite, as either would oxidize arsenite. From a consideration, however, of the action of other alkalies and of hot solutions of ammonia on nitrogen iodide and also of the action of ammonia on solutions of hypoiodites, it is almost certain that the solution contains hypoiodite.

the equation  $kx.w.c'' = (c')^3$  should apply to the state of equilibrium, where  $x$  = the concentration of the solid nitrogen iodide (which is constant),  $w$  = the concentration of the water (which is very large and does not appreciably vary),  $c''$  that of the  $\text{NH}_4\text{OH}$ ,  $c'$  that of the  $\text{NH}_4\text{OI}$ . Then  $\frac{(c')^3}{c''} = k.x.w = \text{a constant}$ .

The following table gives the results of experiments with four concentrations of ammonia at a temperature of  $12^\circ \text{C}$ .

Concentration of ammonia in gram-molecules per liter = $c''$ .	Concentration of hypiodite in gram-molecules per liter = $c'$ .	$(c')^3$ .	$\frac{(c')^3}{c''}$ .
0.1	0.00023	$0.012 \times 10^{-18}$	$0.12 \times 10^{-8}$
0.5	0.000385	$0.060 \times 10^{-18}$	$0.12 \times 10^{-8}$
1.0	0.000525	$0.14 \times 10^{-18}$	$0.14 \times 10^{-8}$
3.0	0.0007	$0.33 \times 10^{-18}$	$0.11 \times 10^{-8}$

The value of  $c'$  is, however, so extremely small that little stress can be laid on the results. They confirm, however, so far as they go the above explanation.

There is very little direct evidence from which to deduce a constitutional formula for this so-called nitrogen iodide. It may be supposed with a fair degree of certainty that the two nitrogen atoms are linked together, and that the compound is represented by one of the formulæ,  $\text{NH}_3 : \text{NI}_3$  or  $\text{NH}_2\text{I} : \text{NHI}_2$ .

All the evidence we have goes to show that the former is the more likely. Nitrogen iodide, which has been allowed to stand under water, becomes much more liable to explode, and analyses of partly decomposed material point to a disintegration of the molecule and a liberation of very unstable  $\text{NI}_3$  in the residue, but this latter compound cannot be isolated, and only exists, if at all, in the presence of a large excess of free iodine.

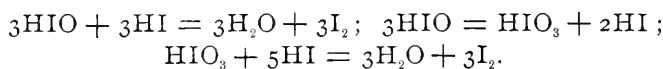
#### EXPERIMENTAL PART.

##### *Action of Iodine on a Solution of Ammonia.*

In these experiments we employed an approximately decinormal solution of iodine in chloroform. Solutions of iodine in potassium iodide led to inexact results, owing probably to the large excess of iodide necessarily present.<sup>1</sup> A known

<sup>1</sup> It was stated (J. Chem. Soc., 1896) that more than half the iodine used could, under certain conditions, be converted into nitrogen iodide. This is not correct. The error was caused by the use of a solution of iodine in potassium iodide.

quantity of the chloroform solution was run into a known quantity of a solution of ammonia. The flask containing the mixture was shielded carefully from the light and shaken for two or three minutes. The nitrogen iodide was then filtered off through ignited asbestos by the help of a filter-pump and washed three or four times with water. The iodine in the nitrogen iodide was estimated by standard sodium sulphite. The filtrate was acidified and the iodine set free titrated. It is a measure of the hypiodite remaining after the nitrogen iodide is precipitated, and is independent of the transformation into iodate and iodide, as is shown by the following equations :



Amount of iodine used as cubic centimeters of a decinormal solution.	Amount of 3.3 N solution of ammonia used.	Amount of iodine in nitrogen iodide expressed as cubic centimeters of a decinormal solution.	Amount of iodine in ammonium hypiodite expressed as cubic centimeters of a decinormal solution.	Total amount of iodine in nitrogen iodide and in ammonium hypiodite expressed as cubic centimeters of a decinormal solution.	Half amount of iodine used.
51.6	20	24.6	1.1	25.7	25.8
48.4	20	23.6	0.6	24.2	24.2
41.2	40	19.8	0.8	20.6	20.6

The agreement between columns 5 and 6 is very good. In the interaction of iodine and ammonium hydroxide, therefore, one-half the iodine becomes initially ammonium iodide and half ammonium hypiodite and nitrogen iodide.

#### *Action of Iodine Monochloride on Ammonia.*

A known quantity of a half-normal solution of iodine monochloride was run into a known quantity of a 3.3 N-solution of ammonia. The solution was screened from light and shaken for two or three minutes. The nitrogen iodide was then filtered off and the iodine estimated in it and in the filtrate as previously described.

Iodine contained in iodine monochloride used expressed as cubic centimeters of a decinormal solution.	Amount of 3.3 N-ammonia solution used.	Amount of iodine in nitrogen iodide produced expressed as cubic centimeters of a decinormal solution.	Amount of iodine in ammonium hypoiodite produced expressed as cubic centimeters of a decinormal solution.	Total amount of iodine in nitrogen iodide and in ammonium hypoiodite expressed as cubic centimeters of a decinormal solution.
23.6	20	22.5	1.1	23.6

A large number of experiments gave exactly similar results. The agreement of columns 1 and 5 shows that the whole of the iodine becomes nitrogen iodide and ammonium hypoiodite.

*Action of Ammonia on a Solution of Potassium Hypoiodite.*

The addition of ammonia to alkaline solutions of potassium hypoiodite, leads under suitable conditions to an immediate separation of nitrogen iodide. When the concentration of the hypoiodite is within certain limits (below 0.03 and above 0.007 gram-molecule per liter) the nitrogen iodide is deposited in the crystalline form.

In these experiments we estimated the amount of hypoiodite in the original solution before the addition of ammonia, and in the alkaline filtrate after the nitrogen iodide had been removed. A standard solution of sodium arsenite was employed to estimate the hypoiodite. This oxidation of arsenite by hypoiodite was noted by Lonnes and used by him in the estimation of the latter.

A liter of the alkaline hypoiodite solution was made up by adding a solution of iodine monochloride in hydrochloric acid to a solution of potash, the latter being in large excess. The alkalinity of the mixture was that of a 3 N/10 solution. At intervals two quantities, each of 100 cc., were simultaneously withdrawn. One was immediately titrated by standard arsenite and to the other 10 cc. of 0.880 ammonia solution were added. After standing for two minutes in the dark, the nitrogen iodide was filtered off and washed with

water two or three times. The hypoiodite in the filtrate and the iodine in the nitrogen iodide formed were then quickly estimated in the same manner.<sup>1</sup>

Concentration of KOH in gram-molecules per liter.	Iodine present in 100 cc. as hypoiodite before addition of ammonia in cc. of $\frac{N}{10}$ solution.	Iodine present in nitrogen iodide obtained from 100 cc. of KOI solution in cc. of $\frac{N}{10}$ solution = <i>a</i> .	Iodine present as hypoiodite in filtrate from the nitrogen iodide in cc. of $\frac{N}{10}$ solution = <i>b</i> .	( <i>a</i> + <i>b</i> ) = iodine present as hypoiodite + iodine in nitrogen iodide in cc. of $\frac{N}{10}$ solution.
0.3	16.8	10.1	6.4	16.5
0.3	8.05	0.85	6.9	7.75

The numbers in column 2 should equal those in column 5. The latter are always a little too low. This would be expected from the loss of hypoiodite unavoidably incurred through conversion into iodate and iodide in the time occupied in filtering off the nitrogen iodide and titrating the filtrate. It is very clear, however, that the nitrogen iodide is formed at the expense of the hypoiodite. The precipitation of the former is accompanied by a proportional decrease of the latter in the solution.

Many experiments have been made with exactly similar results. The influence of alteration in the relative proportions of the potassium and ammonium hydroxides show that, as the concentration of the ammonia increases until the ammonia and potash are in equivalent proportions, the yield of nitrogen iodide rapidly increases. With further increase of the quantity of ammonia the yield of nitrogen iodide slowly reaches a maximum and then falls off. A large excess of potash exercises only a slight influence on the yield, provided the ammonia is present in equivalent excess. In the preparation of the solution of hypoiodite, it has been found that if the admixture of the solutions of iodine monochloride and potassium hydroxide is made with sufficient care and rapidity, no iodine is set

<sup>1</sup> It has been found that solutions of ammonium hypoiodite are converted very slowly into iodate and iodide, some weeks being required for the complete disappearance of the hypoiodite. They offer a marked contrast to solutions of potassium hypoiodite, which completely decompose in twenty-four hours.

free, and the whole of the iodine is for a short time present as hypoiodite. In the experiments, the results of which are given in the following table, the solution of ammonia was added to the hypoiodite solution within fifteen seconds of its preparation. After standing for two minutes the nitrogen iodide was filtered off and estimated.

Concentration of KOH in gram-molecules per liter.	Iodine as hypoiodite present at moment of adding ammonia in cc. of $\frac{N}{10}$ solution.	Concentration of hypoiodite in gram-molecules per liter.	Concentration of ammonia in gram-molecules per liter.	Iodine in nitrogen iodide obtained in cc. of $\frac{N}{10}$ solution.	Percentage of iodine used which was converted into nitrogen iodide.
0.40	35.8	0.0358	0.0585	15.4	43.0
0.40	35.8	0.0358	0.117	18.1	50.5
0.40	35.8	0.0358	0.234	22.7	63.3
0.40	28.6	0.0358	0.488	19.2	67.2
0.46	24.0	0.024	0.936	18.2	76.0
0.46	24.0	0.024	1.87	18.1	75.0
0.46	24.0	0.024	6.0	17.4	72.0

In the following table are given the results of several experiments which demonstrate clearly the fact that nitrogen iodide only separates from solutions of alkaline hypoiodites when the concentration of the latter is above a certain value.

Concentration of KOH in gram-molecules per liter.	Iodine as hypoiodite present at moment of adding ammonia in cc. of $\frac{N}{10}$ solution = <i>a</i> .	Concentration of hypoiodite before addition in gram-molecules per liter.	Concentration of ammonia in gram-molecules per liter.	Iodine in nitrogen iodide obtained in cc. of $\frac{N}{10}$ solution = <i>b</i> .	Iodine as hypoiodite after precipitation of nitrogen iodide as cc. of $\frac{N}{10}$ solution = ( <i>a</i> - <i>b</i> ).	Concentration of hypoiodite after precipitation of nitrogen iodide in gram-molecules per liter.
0.3	3.86	0.0038	1.6	0.0	3.8	0.0038
0.54	7.7	0.005	6.0	0.0	7.7	0.005
0.3	8.06	0.0073	1.6	0.85	7.2	0.0065
0.57	16.2	0.015	1.6	8.0	8.2	0.0076

The formation of the nitrogen iodide ceases when the concentration of ammonium hypoiodite in the solution falls to the limit at which it is capable of existing under the conditions. A final state of equilibrium is then established between the potassium and the ammonium hypoiodites, which is only gradually altered by the slow transformation into iodate and iodide.

*Action of Ammonium Hydroxide on Nitrogen Iodide.*

The action of a hot solution of ammonia on nitrogen iodide resembles that of the alkaline hydroxides, the major portion is hydrolyzed, forming finally iodate and iodide, while a smaller part decomposes into nitrogen and hydriodic acid. As ammonium hypoiodite is the first product of the hydrolysis, and as this can, when the concentration is sufficient, transform into nitrogen iodide, on rapidly cooling such a hot solution in which the nitrogen iodide has only just disappeared, crystals of the latter again separate. If the solution be cooled slowly or the boiling continued for a short time, no crystals are deposited, as the hypoiodite at the high temperature is rapidly and completely transformed into iodide and iodate. The following experiments, carried out with a hot solution of ammonia exactly as described under the action of hot potash, show the variable proportion in which the two actions take place :

$\frac{N}{10}$	$\frac{Na_2SO_3}{2}$	Total iodine in nitrogen iodide used as cc. of an $\frac{N}{10}$ solution.	Ratio of iodine as iodate to total iodine.	Percentage of nitrogen iodide decomposed into nitrogen and hydriodic acid.
28.2		16.4	0.859 : 3	14.02
20.6		12.4	0.830 : 3	16.93
31.3		20.1	0.778 : 3	22.13

When nitrogen iodide is suspended in a cold solution of ammonia similar actions take place but very gradually, bubbles of nitrogen are but slowly evolved, and a large quantity of nitrogen iodide remains with little apparent change for months, although an exceedingly slow conversion of nitrogen iodide into ammonium iodide and iodate is continually progressing.

Ammonium hypoiodite, however, appears directly in the solution, and in a short time has attained its maximum con-



centration, which is always very small. The concentration of the hypoiodite increases with rise of temperature and with increased concentration of the ammonium hydroxide. For a given concentration of ammonia and a given temperature, the ultimate concentration of hypoiodite is the same, whether the starting-point is iodine monochloride and ammonia or nitrogen iodide and ammonia.

In the experiments made about 0.5-1 gram of pure crystallized nitrogen iodide was placed in a stoppered bottle containing 300 cc. of a solution of ammonia of known strength. A number of these were allowed to stand in a dark cellar where the temperature did not vary more than 0°.5 for days. At intervals 100 cc. of the supernatant liquid were withdrawn and filtered through ignited asbestos. To estimate the hypoiodite, excess of standard arsenite was added and carbon dioxide was passed in until the smell of ammonia became faint. By means of standard iodine solution, the excess of arsenite was then estimated. Blank experiments, made with solutions of ammonia of the strength used, show that neither the various operations nor the presence of the large quantity of ammonium bicarbonate in any way affected the accuracy of the titration of arsenite by iodine.

Concentration of $\text{NH}_3$ in gram-molecules per liter.	Series I: Nitrogen iodide in contact with solution of $\text{NH}_4\text{OH}$ for twenty-four hours. Temp. = 12° C.		Series II: Nitrogen iodide in contact with solution of $\text{NH}_4\text{OH}$ for three days. Temp. = 12° C.	
	Amount of $\frac{\text{N}}{10}$ arsenite oxidized. cc.	Concentration of hypoiodite in gram-molecules per liter.	Amount of $\frac{\text{N}}{10}$ arsenite oxidized. cc.	Concentration of hypoiodite in gram-molecules per liter.
0.12	0.48	0.00024	0.51	0.00025
0.24	0.55	0.00027	0.56	0.00028
0.48	0.68	0.00034	0.72	0.00036
1.08	1.05	0.00052	0.92	0.00046
2.16	1.50	0.00075	1.53	0.00076
3.0	1.70	0.00085	1.67	0.00083

A comparison of these two series shows the accuracy attainable and the influence of the concentration of ammonia.

Concentration of $\text{NH}_3$ in gram-molecules per liter.	Series III: Nitrogen iodide in contact with a solution of $\text{NH}_4\text{OH}$ for twenty-four hours. Temp. = $12^\circ \text{C}$ .		Series IV: Nitrogen iodide in contact with a solution of $\text{NH}_4\text{OH}$ for one and a half hours. Temp. = $29^\circ \text{C}$ .	
	<div> <div>oxi- arsenite</div> <div> <math>\frac{\text{N}}{10}</math> Amount of dized. cc. </div> </div>		<div> <div>oxi- arsenite</div> <div> <math>\frac{\text{N}}{10}</math> Amount of dized. cc. </div> </div>	
	Concentration of hypoiodite in gram-molecules per liter.		Concentration of hypoiodite in gram-molecules per liter.	
0.1	0.46	0.00023	0.94	0.00047
0.5	0.79	0.00038	1.79	0.00090
1.0	1.05	0.00052	2.24	0.00112
3.0	1.40	0.00070	3.33	0.00167

Series III. and IV. demonstrate the influence of temperature. A rise in temperature of  $17^\circ \text{C}$ . (from  $12^\circ \text{C}$ . to  $29^\circ \text{C}$ .) doubles the concentration of the hypoiodite. As a consequence, on rapidly cooling a few cubic centimeters of the most concentrated ammoniacal solution of hypoiodite, crystals of nitrogen iodide separate.

In the following experiments a solution of iodine monochloride was added to a solution of ammonia, the further procedure being as described above for Series III:

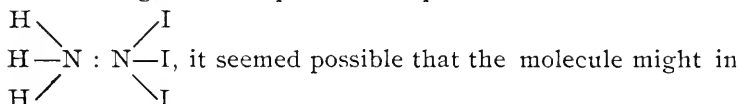
Concentration of $\text{NH}_3$ in gram-molecules per liter.	Amount of $\frac{\text{N}}{10}$ arsenite oxidized. cc.	Concentration of hypoiodite in gram-molecules per liter.
0.088	0.37	0.00019
0.5	0.74	0.00037
1.0	0.97	0.00049
3.0	1.4	0.00070

A comparison of results shows that the same final state of equilibrium is attained whether the starting-point is nitrogen iodide and ammonia or iodine monochloride and ammonia.

*Study of Various Stages in the Decomposition of Nitrogen Iodide by Water and Dilute Sulphuric Acid.*

The actions which take place when nitrogen iodide is completely decomposed by water or dilute acids have already been described. A careful study has been made of the course of these reactions, as it appeared likely to throw light upon the structure of the nitrogen iodide molecule.

Assuming, for example, the compound to have the formula



the first instance break down into  $\text{NI}_3$  and  $\text{NH}_3$  when hydrolyzed by water or dilute acids. The  $\text{NH}_3$  might then be washed away either alone or combined with acid, leaving the  $\text{NI}_3$  as an insoluble residue mixed with still undecomposed nitrogen iodide.

An estimation of the ratio of N to I in the partially decomposed product would then give some information as to the molecular structure.

The problem is complicated by the fact that, in such a partial decomposition, iodine is produced from the first and remains in the insoluble residue. This free iodine can, however, be estimated and the ratio of nitrogen to combined iodine determined in any mixture of compounds, since such combined iodine must be directly attached to the nitrogen in all.<sup>1</sup>

The decomposition of a large quantity of pure nitrogen iodide by water has, therefore, been quantitatively studied. About 0.5 kilogram of the pure amorphous compound was decomposed by water in absence of light. At first it was placed in a large funnel, closed by a plug of asbestos, and water allowed to percolate through the mass. Afterwards, as such partially decomposed nitrogen iodide is extremely sensitive and the local explosions caused by the escape of bubbles of gas become dangerous, it was transferred to a stout porcelain vessel and water allowed to run slowly over it.

At short intervals, at first every few minutes, then every hour, and finally every day, portions were removed, carefully

<sup>1</sup> See "The Composition of Nitrogen Iodide," *This JOURNAL*, 24, 144.

washed and analyzed. Some 80 analyses altogether were made of which a few, typical of different stages of decomposition, are given in the following table in the relative order in which they were made. Similar results are obtained when nitrogen iodide is decomposed by dilute sulphuric acid, although the action is much more rapid :

Number of analysis.	$\frac{N}{10} = \frac{Na_2SO_3}{2} = d.$ cc.	$\frac{N}{10}$ $NH_3$ required to neutralize solution $= \frac{N}{10}$ $HI$ produced in free state.	$\frac{N}{10}$ $AgNO_3$ required $= \frac{N}{10}$ $HI$ formed $= b.$ cc.	$\frac{N}{10}$ $NH_3$ formed. cc.	$\frac{N}{10}$ $I$ present as nitrogen iodide. cc.	$\frac{N}{10}$ $I$ present as free element. cc.	Percentage of total iodine present as free element.	Ratio between $NaI$ in the mixed substances containing $I$ attached to $N$ in the partially decomposed product.
1	93.6	15.6	46.8	31.2	46.8	0.0	0.0	2 : 3
2	36.7	6.7	18.5	11.8	18.2	0.3	1.62	1.94 : 3
3	55.9	10.8	28.2	17.4	27.7	0.5	1.77	1.88 : 3
4	62.3	15.7	31.6	15.9	30.7	0.9	2.85	1.55 : 3
5	86.8	26.6	45.3	18.7	41.5	3.8	8.39	1.35 : 3
6	65.7	28.1	39.4	11.3	26.3	13.1	33.25	1.28 : 3
7	66.6	33.5	42.9	9.4	23.7	19.2	44.78	1.18 : 3

It is seen that the ratio of nitrogen to iodine atoms in the residue, excluding the free element, continually decreases as the decomposition proceeds, and that it slowly approaches the ratio  $N : 3I$  required by the substance  $NI_3$ . This result makes it very probable that the constitution of the molecule really is represented by the formula given above, and that, on decomposition by water or dilute acids, those molecules which do not break down into  $N$  and  $HI$  first decompose into  $NI_3$  and  $NH_3$ , and that the former is then hydrolyzed.

If the ratio  $N : 3I$  could be ultimately obtained, and the results were absolutely to be relied upon, the formula would be established. The large percentage of iodine present when this ratio is nearly reached introduces, however, a possibility of error and, although the constitution  $NH_3 : NI_3$  is rendered very probable, it cannot be regarded as conclusively proved.

In conclusion we desire to thank Mr. R. T. Evans and Mr. W. L. Blackman, who have rendered us great assistance in various parts of the work.

The following is a complete list of previous researches on the subject :

Courtois: *Ann. Chim.*, **88**, 304 (1813); Vauquelin: *Ibid.*, **90**, 239 (1814); Gay-Lussac: *Ibid.*, **91**, 5 (1814); Colin: *Ibid.*, **91**, 252 (1814); Davy: *Ibid.*, **92**, 89, and *Trans. Roy. Soc.*, **86** (1814); Sérullas: *Ann. chim. phys.* [2], **22**, 172 (1825), and **42**, 200 (1829); Mitscherlich: *Gmelin's Chemistry*, Vol. 2, 465; André: *Jour. Pharm.*, **22**, 137 (1836); Millon: *Ann. chim. phys.* [2], **69**, 78 (1838); Marchand: *J. prakt. Chem.*, **19**, 1 (1840); Bineau: *Ann. chim. phys.* [2], **67**, 225 (1836), and [3], **15**, 71 (1845); Cass: *Jour. Pharm. Chim.*, 52 (1851); Bunsen: *Ann. Chem. (Liebig)*, **84**, 1 (1852); Gladstone: *J. Chem. Soc.*, **4**, 34 (1852), and **7**, 51 (1853); Schönbein: *J. prakt. Chem.*, **84**, 385 (1861); Stahlschmidt: *Ann. phys. Chem.*, **29**, 421 (1863); Guthrie: *J. Chem. Soc.*, **16**, 239 (1863); Stas: *Nouvelles Recherches* (Brussels), 1865, p. 157; Champion et Pellet: *Bull. Soc. chim.* [2], **24**, 447 (1875); Mallet: *This JOURNAL*, **1**, 4 (1879-1880); Guyard: *Compt. rend.*, **97**, 526 (1883), and *Ann. chim. phys.* [6], **1**, 358 (1884); Raschig: *Ann. Chem. (Liebig)*, **230**, 212 (1885); Willgerodt: *J. prakt. Chem.*, **145**, 446 (1888); Szuhay: *Ber. d. chem. Ges.*, **26**, 1933 (1893); Seliwanow: *Ibid.*, **27**, 1012 (1894); Chattaway: *J. Chem. Soc.*, 1896, 1572; Losanitsch and Jovitschitsch: *Ber. d. chem. Ges.*, **29**, 2436 (1896); Mallet: *Proc. Chem. Soc.*, 1897, 55.

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## INVESTIGATION OF THE HALPHIN COLOR TEST AS TO ITS VALUE FOR THE DETECTION OF COTTONSEED OIL.

BY ROZIER D. OILAR.

In 1898 there appeared in several of the chemical journals a few brief articles relating to a certain color test for the identification of cottonseed oil, as devised by Mr. Georges Halphin. After confirming the reliability of this reaction by a number of tests at that time, the somewhat modified test was, on account of its simplicity and sensitiveness, adopted by the writer

for the identification of cottonseed oil in oils and fats, in preference to the Becchi and Milleau tests.

Being called upon later, in a commercial way, to defend certain claims as based upon this test, it became apparent that the real value of this reaction was not generally accepted and consequently it has been more thoroughly investigated by the writer to further test its reliability and to secure its more general recognition among chemists.

The few references to the test found in the journals give only its general principles and a few of the results obtained by the respective authors. Halphin first called attention to his reaction in 1894<sup>1</sup> by stating that, from the evaporated distillate from a mixture of fatty acids of a fat or oil, carbon disulphide, and zinc oxide, an amber-yellow residue is obtained with hog, beef, mutton, and goat fats, while, when cottonseed oil is present, an orange-red zinc salt is obtained. He asserted later<sup>2</sup> that this coloration is due to the action of the carbon disulphide rather than the zinc oxide, and further recommended the addition of free sulphur, the whole being dissolved in amyl alcohol, giving as his method of procedure the following: Mix equal parts of oil or fat, amyl alcohol, and carbon disulphide containing 1 per cent free sulphur, and heat in a saturated solution of salt for ten to fifteen minutes. If no color appears, reheat and add more of the carbon disulphide solution.

P. Soltsien<sup>3</sup> states that he has tried Halphin's test, and says that amyl alcohol and the salt-bath are unnecessary. He compares the color to a solution of potassium dichromate, and says that old and rancid fats do not produce the reaction, and that in colorless and clear fats 1 per cent of cottonseed oil can be recognized, while with colored fats from 2 to 5 per cent, according to the depth of color of the original sample. He states that an oil (cottonseed) heated to 200° gives the reaction unchanged, and he gives the following as not showing the coloration: Lard, strongly rancid lard, old rancid lard oil, the same mixed with tallow, sesame oil, various cheese

<sup>1</sup> *CentrbI.*, 1894, II., 716.

<sup>2</sup> *Ibid.*, 1897, II., 1161.

<sup>3</sup> *Ibid.*, I, 1049 (1899).

fats, olive oil, rapeseed oil, poppy oil, camelina (German sesame) oil, cod-liver oil, arachide oil, and hazelnut oil.

D. Holde and R. Pelgry<sup>1</sup> confirm the Halphin reaction, but claim to have got it with thran or blubber oil, quoting Halphin as having obtained a coloration with a pure thran oil, although Halphin says this will not be confounded with the cotton oil coloration, if it is allowed to flow in a thin layer on a stirring rod. They claim that an oil heated to 250° does not give the reaction.

P. Soltsien<sup>2</sup> replies that an oil heated to 250° is no longer fit for use as an edible, but up to 200° the reaction is permanent. He says that the test should be heated from forty-five minutes to one hour to get the full coloration. Holde and Pelgry<sup>3</sup> state that the point of destruction is below 250°, somewhere between 210° and 250°.

L. Archbutt<sup>4</sup> has used the test on maize oil with negative results.

Other references are to be found as noted below.<sup>5</sup>

The writer's work corroborates to a great extent that of the above chemists, but he finds that for the proper coloration the combined action of the carbon disulphide, sulphur, and amyl alcohol is required, and that not one of these can properly be dispensed with as claimed by some. Ordinary ethyl alcohol gives the reaction with less depth of coloration than amyl alcohol, and the salt-bath is most desirable on account of the high constant boiling-point it affords.

We find, as Soltsien did, that old and rancid fats do not produce the reaction, and, further, that an old and rancid cottonseed oil or fat mixture containing it produces a weaker and more brownish reaction, even to the total obliteration of the reaction in very old fats or oils. The Becchi and Milleau tests, on the contrary, are more or less produced by such conditions. Consequently, with the Halphin test, as with other tests, the fresher the material tested the more satisfactory the results.

<sup>1</sup> Centrbl., I., 1085 (1899).

<sup>2</sup> *Ibid.*, I., 1297 (1899).

<sup>3</sup> *Ibid.*

<sup>4</sup> J. Soc. Chem. Ind., April, 1899.

<sup>5</sup> Chem. Rev. Fett. u. Harz-Ind., 6, 67, and 6, 94; Ztschr. öfent. Ch., 5, 106; Revue de chim. Ind., Feb., 1898; Jour. Pharm. Chem. [5], 30-241, and [6], 6, 390; The Analyst, May, '98, 114 and 131; Am. Chem. Analyst, 3, [1] 9-11.

Soltsien has found the test sensitive to 1 per cent of cottonseed oil, while we have been able to obtain a coloration with quite a small fraction of 1 per cent under favorable conditions, *i. e.*, fresh material not too deeply colored.

As to the degree of heat applied to the original oil necessary to destroy the reaction with it, we find it to be influenced by the length of time heated, and the quality of material in contact with the oil. With glass vessels this point of neutralization lies between  $315^{\circ}$  and  $320^{\circ}$  C.,<sup>1</sup> slightly lower in a vacuum, while, if the vessel is of metal or contains pieces of metal, this limit is lowered more or less in proportion to the metal in contact with the oil. As an example, an oil heated half an hour in a porcelain-lined kettle at about  $200^{\circ}$  showed that the reaction was little, if any, affected; while an oil heated in a steel frying pan at  $140^{\circ}$ – $150^{\circ}$  for an hour gave no indication (or coloration) of cottonseed oil. While the metals tend to lower the point of neutralization, they do not bleach a color once produced.

The active ingredient of cottonseed oil is not merely driven off from the oil by high heat, but is completely destroyed, since the fumes arising from it, as well as the oil, give no coloration.

As to the degree of heat that would be detrimental to an oil for culinary purposes, we certainly agree with Soltsien that  $250^{\circ}$  is even excessive. The temperature of an oil for frying should not exceed  $150^{\circ}$ – $160^{\circ}$  (lards and solid fats somewhat lower), at which point it will "brown bread crumbs;" while for frying crullers the temperature will probably rise to  $200^{\circ}$ – $210^{\circ}$ .

The method of procedure, as adopted by the writer, is as follows:

*Apparatus Required.*—10 cc. pipettes (3); test-tubes ( $1\frac{1}{8}$ "  $\times$  8" to 10"); saturated salt-water bath.

*Reagents.*—Amyl alcohol (C. P.); carbon disulphide (C. P.), containing 1 to 2 per cent fresh flowers of sulphur.<sup>2</sup>

*Manipulation.*—10 cc. each of the solutions is measured

<sup>1</sup> Somewhat lower temperature with longer time of heating.

<sup>2</sup> A higher percentage of sulphur does not improve the reaction.



into a test-tube with 10 cc. of the oil or melted fat sample.<sup>1</sup> The mixture is agitated frequently and heated first in a steam-bath until the violent boiling ceases, and then placed in the boiling salt-water bath (temp. 105°-110°) for from forty-five minutes to one hour—two to three hours if only traces of oil are present—occasionally removed and agitated. The steam-bath should be used at first to prevent the first heavy fumes of carbon disulphide from igniting by contact with the open flame.

*Indications.*—A beautiful crimson wine coloration, varying in depth according to the percentage of cottonseed oil present. If no coloration appears after two to three hours' boiling, the sample contains no cottonseed oil, while as little as 1 per cent will give indications in fifteen to twenty minutes.

If heated over four to five hours, a misleading brownish-red color is produced, even with pure lard, a result which is due to burning.

Necessarily, the first thing to be determined was whether the test is characteristic of cottonseed oil, and that alone among the various fats and oils; second, whether any compound, organic or inorganic, probably present in commercial fats and oils, such as fillers and colorings, will produce this reaction; and, third, the sensitiveness of the reaction with cottonseed oil in other fats.

Of the various fats and oils examined by the writer with this test, samples of four other oils than cottonseed oil have given colorations somewhat resembling that of the cottonseed oil reaction. These colorations were of a brownish or yellowish shade and were barely noticeable with a 5 per cent mixture in (C. P.)<sup>2</sup> lard, showing that, as far as these samples go, it is not a very delicate test for the oils mentioned. These four samples of sunflower, rape or colza, nigre, and poppyseed oils of foreign manufacture, as purchased in the open market and, consequently, of uncertified purity, gave, as noted, more or less of a coloration; but, when these same oils were extracted with rectified gasoline directly from their unadulterated seeds (with the exception of rape oil, which

<sup>1</sup> Five cc. each is used in routine daily tests, any indication being verified by taking 10 cc.

<sup>2</sup> By C. P. lard is meant lard free from any cotton oil.

seed could not be obtained), thereby insuring absolute freedom from contamination with other oils, no coloration whatever was noticed after several hours.<sup>1</sup>

It would appear from this that the samples showing colorations were not of the purest quality and contained traces of cottonseed oil, which assumption is further strengthened by observations on other samples of rape and poppy oil, which gave no reaction, and also by Soltsien's<sup>2</sup> negative results with them. As the method of alternating pressings of various kinds of oil seeds as practiced in most European mills, would permit of such unobserved sophistication, it seems more than probable that cottonseed oil would become more or less mixed with the various other oils in the process of manufacture, and thus give one the apparently misleading indication with the other oils. It has been found to the manufacturer's sorrow, if the Halphin test is used, next to an impossibility to handle cottonseed oil and other oils and fats through the same presses, pumps, pipes, tanks, etc., and to keep the various oils and fats free from traces of the cottonseed oil, however much care is used in rinsing out the apparatus.

I. It seems then fairly evident that the Halphin reaction is produced by none of the common edible oils and fats other than that from the cottonseed.<sup>3</sup>

II. Using the test mostly in connection with (hog) lards, we have used that fat as a medium for adulterants, mixing with such lards as give no trace of a reaction, various fillers and colorings; as yet we have found nothing tending to give the reaction,<sup>4</sup> thus establishing it as still more reliable as a characteristic test of cottonseed oil.

III. As to the sensitiveness of the reaction or the percentage of cottonseed oil shown by this test we have found it decidedly positive in lards with 1 per cent, and without doubt reliable with  $\frac{1}{2}$  and even  $\frac{1}{4}$  per cent; also  $\frac{1}{8}$  to  $\frac{1}{10}$  and even  $\frac{1}{100}$  per cent of cottonseed oil in fresh colorless lards gives a noticeable faint coloration if compared with a blank test (one with a pure lard).<sup>5</sup>

<sup>1</sup> See Table I.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> See Table I.

<sup>4</sup> See Table II.

<sup>5</sup> See Table III.

Of the various grades of cottonseed oil the test works with crude, yellow, and white; and summer, winter, and (oil) stearin qualities almost equally well, being darker with the crude, and scarcely noticeably so with the yellow, than with the white, due to the original additional color; and lighter with the oil stearin, and slightly so with the summer, than with the winter, oil, indicating that the active principle of the oil is not contained in the triglycerides of stearic acid.

This test can be used more or less quantitatively by comparing, in small tubes, the depths of color produced with those of equally concentrated volumes from tests of mixtures of known percentages of oil (most satisfactorily in lards with mixtures of less than 1 per cent cotton oil).

The coloration produced by this reaction is quite stable in the dark, being only slowly affected by exposure to light and air.

A cottonseed oil or fat mixture containing a high percentage of this oil, treated with the Halphin solutions and once colored retains the color in its soap, fading after a time, and even in its fatty acids, only a small portion washing out from the fat.

This test can be applied directly to the soap or fatty acids of a fat mixture of high percentage of cotton oil if not too deeply colored, with some degree of confidence, the coloration produced being more brownish than with the neutral fat, and consequently not as delicate a reaction. The subjection of the fatty acids to an oven temperature of  $100^{\circ}$  affects the results only slightly with the higher adulterations of oil, while with the lower percentages it destroys the colorations more or less through the darkening of the acids themselves.

This reaction may be made use of to some extent in inorganic work for the recognition of free sulphur, by treating the unknown substance with a mixture of equal parts of pure cotton seed oil (bleached), amyl alcohol, and carbon disulphide free from sulphur.<sup>1</sup>

As to the active principle or compound in cottonseed oil that produces the Halphin reaction, technically it is not of so great importance, although scientifically it might be of con-

<sup>1</sup> See Table V.

siderable interest. As noted, it appears not to be contained in the stearin constituents, is influenced by the action of metals, and is destroyed by high heat, age, and decomposition. The color produced may be due to the same cause as is thought by some to produce the Becchi and Milleau reactions—volatile sulphur compounds contained in the oil; but, as Dupont and Charabut have found sulphur in olive oil, which is neutral to this test, this theory appears less probable.

Following are the tabulated results of a series of experiments which furnish the basis of the foregoing statements:

TABLE I.

### Results with Various Oils and Fats.

Sample of Olive oil	Marked (A) Olive oil (B) "	Purchased at France	Condition.	Coloration produced.
" "	" "	"	Fresh	None other than greenish cast
" "	" "	New York	"	None other than greenish cast
" "	" "	"	Old	None other than greenish cast
" "	Baum Oel	"	"	No pinkish coloration
" "	Huile D'Olive	Marscilles	"	" "
" "	" "	"	"	" "
" "	Provincer oil	"	"	" "
Peanut oil	Arachide oil	France	Fresh	" "
" "	" "	"	Fairly fresh	" "
" "	" "	"	Old	{ Slightly more yellowish
" "	Huile D'Arachides	Bombay	"	{ No pinkish coloration
" "	" "	Mozambique	"	" "
" "	Arachides (extra raffisque)	"	"	{ Faintly yellowish
Sesame oil	Sesami oil	France	Fresh	{ No pinkish coloration
" "	" "	N. Y.	"	" "
" "	Sesam Oel	"	Old	" "

TABLE I (Continued).

Sample of	Marked	Purchased at	Condition.	Coloration produced.
Sesame oil	Sesami oil	?	Old	No pinkish coloration
" "	Sesame	Bombay	"	"
" "	Sesames (extra Jaffa)	?	"	"
" "	Sesame (Brunede Mai)	?	"	"
Corn oil	Corn oil	N. Y.	Fresh	"
" "	" "	Chicago	Old	"
Palm oil	Palm oil	?	"	"
Cocoanut oil	Coprah	India	Fresh	"
" "	Pure cocoanut oil	P. F. P. Co. <sup>1</sup>	Old	"
Linseed oil	Linseed oil	N. Y.	Fresh	"
" "	Lein oil	?	Old	"
Nigre oil	Nigreseed oil	France	Fresh	Brownish, pinkish coloration
5 per cent of above	In (C. P.) lard			Very faint pinkish coloration
Sunflower oil	Sunflowerseed oil	?	Old	Yellowish, pinkish coloration
5 per cent of above	In (C. P.) lard			Brownish-pink, not a positive reaction
Sunflower oil	Sunflower oil	?	Old	Yellowish, pinkish coloration
5 per cent of above	In (C. P.) lard			Practically no coloration

<sup>1</sup> Pure Food Product Co., Chicago, Ill.

TABLE I (*Continued*).

Sample of	Marked	Purchased at	Condition.	Coloration produced.
♂ 24 Sunflower oil	Sonnenblumen Oel	?	Old	{ Brownish-pink colorat'n { (Milleau—Reddish) Practically no coloration
5 per cent of above in (C. P.) lard				
Sunflower oil	Extracted from seed	N. Y.	Fresh	{ No coloration { (Milleau—No col'rat'n)
Rape or colza oil	Rape seed oil	N. Y.	Fresh	{ Slightly brownish-pink { (Milleau—Brownish coloration)
5 per cent of above in (C. P.) lard				
Rape or colza oil	Huile de Navetto	?	Old	Practically no coloration
" "	Extracted from seed	N. Y.	Fresh (A) and (B)	No coloration No coloration whatever { Brownish-yellow; not a { C. S. oil coloration { (Milleau—Reddish coloration)
Poppyseed oil	Mohn Oel	?	Old	Practically no coloration
5 per cent of above in (C. P.) lard				
Poppyseed oil	Pavot de l'Inde	?	Old	No coloration
" "	Extracted from seed	N. Y.	Fresh	No coloration whatever
(Cow) butter	Butter	Local stores	Fresh	No coloration.
" "	" "	Elgin make	?	Coloring in butter masks any coloration possibly produced
" "	" "			No coloration
Beef fat	Tallow (Prime)	Home-made Chicago	Fresh "	No change from original color
" "	" (No. 1)	"	"	No change from original color
" "	Oleo Stearine	"	"	No pinkish coloration
Hog fat	Lard (Prime Steam) <sup>1</sup>	"	"	" "

<sup>1</sup> Of about 500 commercial samples with this method only 5 or 6 gave colorations.

TABLE I (Continued).

Sample of	Marked	Purchased at	Condition.	Coloration produced.
Cottonseed oil	C. S. oil, 'White'	American Mills	Fresh	Deep crimson coloration
"	" " 'Yellow'	"	"	Deep crimson coloration (slightly darker than above)
"	" " 'Crude'	"	"	Deep crimson coloration (darker than above)
"	" " 'Winter'	"	"	Deep crimson coloration
"	" " 'Summer'	"	"	Deep crimson coloration (slightly lighter than above)
"	" " 'Stearine'	"	"	Deep crimson coloration (lighter than above)
"	Extracted from seed	"	"	Deep crimson coloration
"	C. S. oil	"	Old (7 years)	No pinkish coloration
"	" "	"	" (5½ " )	Reddish-yellow coloration, not proper cotton oil coloration
"	Cotton oil stearine	English Mills	Old (decomposed)	No coloration
Rosin oil	Rosin oil	?	?	No change in color
Mineral oil	Oil petrole	N. Y.	Fresh	" " " "
"	Vaseline oil	?	Old	" " " "
Dégrads	Dégrads	?	?	" " " "
Engine oil	Engine oil	N. Y.	Fresh	" " " "
Thran or blubber oil	Menhaden oil	"	?	" " " "
				Deep scarlet coloration (slightly more yellowish than with oil).
Soap	From cotton oil	American Mills	Fresh	Deep scarlet coloration (slightly more brownish than with oil)
Fatty acids	From above	"	(Undried)	



TABLE II.

*Results with Pure Lards and Adulterants, Etc.*

Sample of	Coloration produced.
Pure lard	No coloration
Soap from pure lard	No coloration (other than the cream color of soap)
Fatty acids from above	No coloration (other than the cream color of acids)
Pure lard blown with air, 10 hours <sup>1</sup>	Yellowish coloration after 6 to 7 hours boiling
Pure lard blown with air, 18 hours	Yellowish coloration after 6 to 7 hours boiling
Pure lard blown with air, 24 hours <sup>2</sup>	Slightly cream coloration in 5-6 hours (continued boiling gives maroon color—abnormal test)
Pure lard containing starch	No coloration
“ “ “ resin (Colophony)	“ “
Pure lard containing glycerin	“ “
“ “ “ chlorophyll	“ change in color
“ “ “ Fuller's earth	“ coloration
Pure lard containing salt (NaCl)	“ “
Pure lard containing chlorine (Cl)	“ “
Pure lard containing boric acid	“ “
Pure lard containing salicylic acid	“ “
“ “ “ curcuma	“ “
“ “ “ annatto	“ “
“ “ “ “ carrotene ”	“ change in color
“ “ “ saffron leaves	“ “ “ “
“ “ “ “ annatolene”	“ “ “ “
“ “ “ yellow wood	“ coloration
“ “ “ butter color	“ “
“ “ R”	“ change in color
Pure lard containing butter color “ Y”	“ “ “ “
Pure lard containing oleaginous annatto	“ “ “ “

<sup>1</sup> Free fatty acids, 0.9 per cent.<sup>2</sup> Free fatty acids, 6.2 per cent.

TABLE III.

*Results as to Sensitiveness of Reaction.*

Sample of	Time of test.	Coloration produced.
Pure lard <sup>1</sup>	3-4 hours	No coloration
" "	10 hours	Maroon coloration, not that of a cotton oil (due to overheating—abnormal test)
" "	15 minutes	A pink coloration
" "	15 "	" "
" "	30 "	Quite reddish coloration
" "	15-30 minutes	Faint coloration
" "	2½-3 hours	" "
" "	" "	Very faint coloration
" "	3 hours	Doubtful
" "	4-5 hours	Slight pinkish coloration as compared with blank
" "	15-30 minutes	No color in steam-bath
" "	" "	Quite pinkish in salt-bath
" "	" "	Pinkish in steam-bath in few minutes
" cottonseed oil	" "	Brownish-yellow coloration, no positive indication
Soap from lard with 1 per cent C. S. oil	2-3 hours	No coloration other than that of acids
Fatty acids from above	" "	Brownish-red, not good C. S. oil coloration
Soap from lard with 2 per cent C. S. oil	" "	Not a positive indication
Fatty acids from above	" "	Pinkish in few minutes
Lard with 2 per cent C. S. oil	" "	" "
Compound lard (high per cent C. S. oil)	" "	" "
Soap from above	" "	Reddish-yellow to scarlet, fairly good indication
Fatty acids from above	" "	Deep scarlet, very good indication
" Cottolene" lard compound	" "	{ Deep scarlet color
4-5 years old, center of package	" "	{ Yellowish-red, not a good positive indication
Above sample, surface of package	" "	

<sup>1</sup> See foot-note, p. 365.

TABLE IV.

*Effect of High Temperatures.*

Sample of	Temperature subjected to.	Time held.	Quality of vessel.	Coloration produced.
Cottonseed oil	150° C.	0 <sup>1</sup>	Glass	Normal deep coloration
"	150° C.	$\frac{1}{2}$ -1 hour	"	Doubtfully lighter coloration than above
Above sample	175° C.	0	"	Same as above
"	175° C.	$\frac{1}{2}$ -1 hour	"	" "
"	200°	0	"	About same as above
"	200°	1-2 hours	"	Considerably lighter coloration than above
"	225°	0	"	Still lighter and yellowish, not a good coloration
1 per cent C. S. oil in lard	Normal		"	Good indication
1 "	150°	0	"	Doubtfully lighter reaction
Above sample	150°	$\frac{1}{2}$ -1 hour	"	Same as above
"	175°	0	"	Faintly lighter reaction than above
"	175°	$\frac{1}{2}$ -1 hour	"	Considerably lighter reaction than above
"	200°	0	"	Only faint coloration (2-3 hours boiling)
"	200°	$\frac{1}{2}$ -1 hour	"	No coloration (identity of oil destroyed)
Fresh sample oil	250°	0	"	Possibly lighter reaction than with original oil

<sup>1</sup> Merely brought up to the temperature, not held there.

TABLE IV (Continued).

Sample of	Temperature subjected to.	Time held.	Quality of vessel.	Coloration produced.
Fresh sample oil	275°	0	Glass	Slightly lighter reaction than above
" "	300°	0	"	Somewhat " "
" "	300°	15-30 minutes	"	No coloration (identity of oil destroyed)
Fumes from above				
Fresh sample oil	315°	0	"	No coloration
" "	320°	0	"	Only slight coloration
" "	325°	0	"	No coloration
" "	308°	0	"	" " (after 1 hour boiling)
" "	315°	0	Glass (in vacuum)	Fairly strong coloration
" "	250°	0	"	No coloration
" "	275°	0	Nickel	Faint coloration
" "	275°	0	"	No coloration
" "	295°	0	"	" "
" "	275°	0	Iron	Strong coloration
" "	300°	0	"	No coloration
" "	140°-150°	1 hour	Steel	" "
" "	200°-210°	1 "	Porcelain	Good coloration, little affected
Fresh sample oil + pieces of copper	175°	0	Glass	Coloration
Fresh sample oil + pieces of copper	200°	0	"	No coloration
Fresh sample oil + pieces of iron	285°	0	"	Only slight coloration
" " +	308°	0	"	No coloration

<sup>1</sup> After frying batch of crullers.

TABLE IV (Continued).

Sample of	Temperature subjected to.	Time held.	Quality of vessel.	Coloration produced.
Fatty acids of C. S. oil	110°	12 hours	Glass	Only slightly lighter reaction than undried acids
“ “ 1 per cent C. S. oil in lard	Normal		“	No positive indication
Fatty acids of 1 per cent C. S. oil in lard	110°	12 “		No indication of cotton oil (acids darkened)
Fatty acids from C. S. oil soap stock	Distilled	?	?	No indication of cotton oil
Cottonseed oil	“	?	Glass	“ “ “ “

TABLE V.

*Miscellaneous Experiments.*

Experiment.	Coloration produced.
Cottonseed oil + amyl alcohol ( $C_5H_{11}OH$ ) boiled	No coloration
" + $CS_2$ (pure) boiled	"
" + " + 1 per cent S boiled	Slight coloration (yellowish-brown)
" + " + 1 " S + ethyl alcohol	
( $C_2H_5OH$ ) boiled	Better coloration, not the vivid coloration
Cottonseed oil + ( $CS_2$ + 1 per cent S) + amyl alcohol boiled	Good characteristic coloration
(Lard + 1 per cent C. S. oil) + ( $CS_2$ + 1 per cent S) boiled	No coloration
(Lard + 1 per cent C. S. oil) + ( $CS_2$ + 1 per cent S) + $C_2H_5OH$ boiled	"
(Lard + 1 per cent C. S. oil) + ( $CS_2$ + 1 per cent S) + $C_2H_{11}OH$ boiled	Good reaction
C. S. oil + $C_2H_{11}OH$ + $CS_2$ (pure) boiled	Only pale coloration
Above test + free S boiled	Deep coloration
C. S. oil + $C_2H_{11}OH$ boiled	No
Above + free S boiled	"
" + $CS_2$ boiled	Deep coloration
1 per cent C. S. oil in lard, regular test	Good
1 " " " + 5 per cent S regular test	No improvement in coloration
C. S. oil, regular test	Deep coloration
Above test + copper and boiling	No change of coloration
C. S. oil blown with air several hours regular test	" " of reaction

From the foregoing it appears that the Halphin test, if conducted properly, proves to be thoroughly characteristic of cottonseed oil and is evidently one of the most valuable color tests known for the identification of cotton oil in other oils and fats.

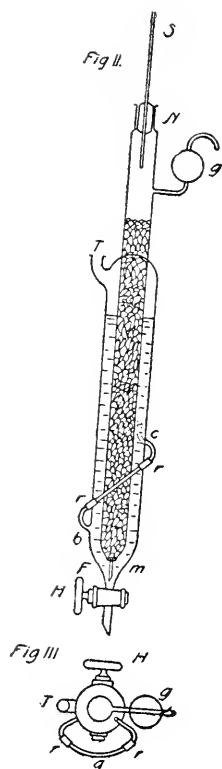
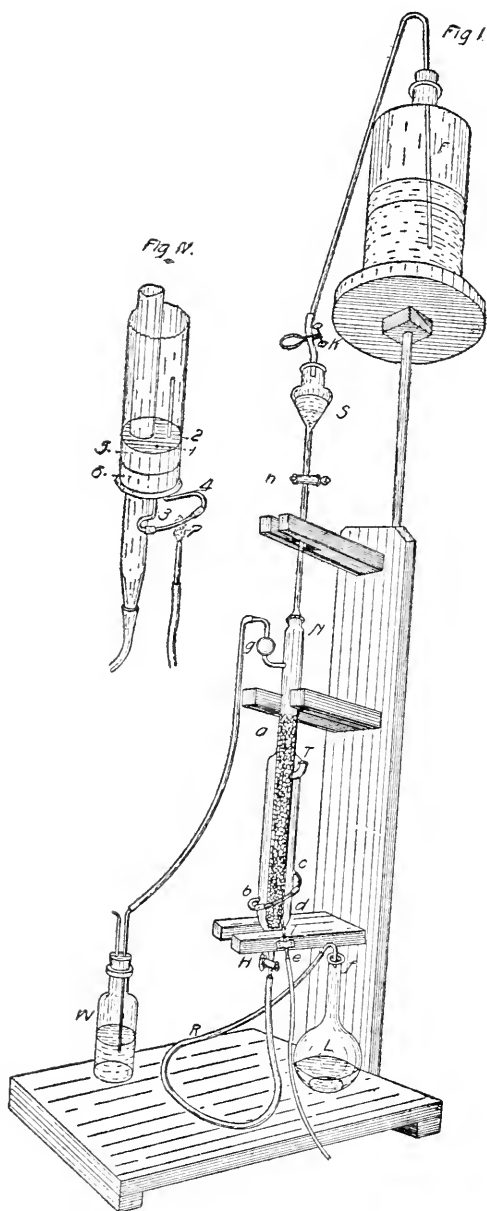
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## APPARATUS FOR GENERATING GASES AT CONSTANT FLOW AND OF HIGH EFFICIENCY.

BY GEORGE A. KOENIG.

The question of how to supply school laboratories with hydrogen sulphide in the least objectionable way is still open for discussion. Many of the best equipped laboratories have each desk provided with the gas in a well-ventilated small hood. Aside from the first cost of such an arrangement, it seems to me to tend to wastefulness on the part of the student. He detaches the rubber tube but forgets the closing of the stop-cock. Or he may let the gas go through a solution for hours, when a few minutes would have been sufficient. Similar objection attaches to the Kipp apparatus in addition to the variation in the flow of gas and the imperfect utilization of the acid. In recent years several styles of apparatus have been described which mark good progress in the right direction. There is, however, still room for improvement. When I took charge of the Department of Chemistry in the Michigan College of Mines, in 1892, I found the laboratories very imperfectly ventilated: the Kipp apparatus in the same hood that served for evaporations, and frequently no draught in that hood. A radical change was too expensive to be practical at the time. Two hoods were put into each laboratory 8 inches deep and 6 feet wide, the draught pipes leading directly near the ridge pole of the building. Draught was created by one burner at the throat of the hood. This arrangement satisfied the demand of ventilation fairly well. In order to counteract the waste of the materials in the Kipp, each hood was provided with two generators essentially of the form shown in the figures: 1. A narrow glass tube 350 mm. long, drawn to about 8 mm. at the bottom. At the top a two-





hole rubber stopper with the stem of a separatory funnel through one hole and a gas delivery tube through the second hole. The stem is about 200 mm. from stop-cock to outflow. On the length of this stem depends the possible inside pressure; the length mentioned satisfies all laboratory demands. The lower end is furnished with the rubber U-tube *R*, Fig. I., and the tube must be sufficiently long to permit a difference of level equal to the length of the stem of the separatory funnel. The generating tube is provided with a disk of copper wire gauze and stem at *m*, Fig. II., and then filled with ferrous sulphide. Now, if the bulb of the funnel *s* holds 50 cc., it is evident that no more acid can be wasted than one filling without refilling the bulb by pressing on the pinch-cock *k*, Fig. I. The stop-cock *h* regulates the outflow of the acid. Here the student may wilfully waste by turning on full instead of 1 drop a second. But he cannot waste much. In fact the gas will be generated so violently, if he turns on full, that he will become alarmed, as I have noticed on several occasions, and he will turn off in most cases. The outflow of the stem should be drawn to 1 mm., in order that a small drop may form. Were it not for the unavoidable minute solids in the dilute acid, a narrowing to 0.5 mm. would be preferable. This clogging happens mostly in the stop-cock *s*, and is the only objectionable feature in my scheme. In most cases a quick turn to full flow, several times repeated, will remove the clogging matter; but sometimes the pushing through of a thin wire is needed.

The hot-water jacket was added in the first place for generating chlorine gas with this apparatus. But last winter, in February, when the temperature of the rooms fell to near freezing-point during the night, the hydrogen sulphide generators refused to start in the morning, the dilute cold acid being without effect upon the iron sulphide, then the jacket was added. The result has been so satisfactory that a temperature of about 80° C. is maintained now in all generators. The water-jacket should be of glass; spilling of acid is unavoidable, and corrosion of any metallic tube would be certain; moreover, the decrease in the column of ferrous sulphide should be visible.

Fig. IV. shows a simple way of constructing a tight jacket. The generating tube being 25 mm. wide, the jacket tube is 45 mm. The rim of the latter is flared outwards. A cork stopper (5) is fitted to slide into the tube tightly. The stopper is bored eccentrically for the generator tube, leaving room for the small borings (1) and (2). Push this stopper into position, 30 mm. above the rim, insert the generator tube and the small tubes so that (1-3) is just even with the inner disk, whilst (2-4) projects above this disk about 40 mm. Either tube is bent at right angles, the one at (3) the other at (4), and there is a second short bend so that the piece 9 can be inserted between the ends by means of short rubber connections (*z, z*, Fig. III.). 9 is bent to be concentric with the jacket, and must stand off at least 30 mm. The bend at (3) is 25 mm. below the rim of the jacket, whilst bend (4) is tangent to it. The piece (9) is about 80 mm. long and 5 mm. wide (outer diameter). This piece, after being fitted into place, forms an incline (Fig. II.). When all the pieces are in proper position, reverse the tube and pour into the space (6) properly moistened Portland cement of the consistency of thick mud. Stir it carefully with a wire to remove air bubbles, and set away two days. Neither sealing wax nor plaster of Paris answer the purpose. Portland cement stands the hot water indefinitely. The upper end of the jacket is best protected by a roof of sheet aluminum against the spilling of acid, which would soon destroy the cement block at the bottom. The roof can be fastened to the generator tube by a rubber band.

The jacket being filled with water, we place a small flame (7) under the boiling-tube (9). (This latter is best made of brass, although I find that a glass tube stands a long time with proper care.) It is evident that a warm water current is established at once, the cold water sinking into (1) and the hot water rising through (2) to the upper jacket. The burner consists of a 5 mm. glass tube and the flame is about 12 mm. high, later only 6 mm., when the jacket has assumed the proper temperature. Figs. I., II., and III. represent the apparatus entirely of glass. The rubber stopper is done away with, its place being taken by a ground glass stopper *N*, which is melted into the stem of the separatory funnel. The ar-

rangement of the boiling tube explains itself from the drawing. Generating tube and jacket are fused together above and below. The tubulature (*T*) serves to fill water into the jacket. The glass stop-cock (*H*) at the outflow of the generating tube was introduced to do away with the rubber tube *R*. This was not found to be feasible, because the very narrow opening fills up at once with the fine particles of the generating body. The bore in the cock must not be under 5 mm. This stop-cock has proved serviceable in other ways. Whenever the apparatus is to be taken from the stand the cock is closed and all dripping from the rubber tube is thus avoided.

The iron sulphide should be screened after crushing or granulating, and only those pieces should be charged into the generator whose average diameter lies between 3 mm. and 10 mm. The charging is done with a funnel made from sheet aluminum after lifting out the stopper at *N*. The tube being filled up to the goose-neck, the apparatus will work steadily for one working day without perceptible lessening of the constancy of the gas current, although the economy in acid will diminish. The tubes in my laboratories are charged every morning.

When the apparatus is to be used for the generation of chlorine, the column of manganese dioxide should not be higher than one-third of the available tube. The concentrated hydrogen chloride should be diluted with enough water to raise the boiling-point to 80° C. Under such conditions a chlorine current can be maintained of extraordinary constancy. The pyrolusite should be screened to pieces between 2 mm. and 5 mm.

MICHIGAN COLLEGE OF MINES,  
June, 1900.

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## REPORT.

### *International Atomic Weights.*

Near the close of the year 1897, the German Chemical Society appointed a committee to select atomic weights for common use in Germany. The confusion arising from the use of different values, and especially of different standards of reference, had become unbearable. After nearly

a year's deliberation, they announced their conclusion that it is expedient to call oxygen exactly 16, and to refer other elements to this standard. They published a carefully considered and conservative table of atomic weights,<sup>1</sup> which immediately gained wide acceptance, partly because of its intrinsic merits, and partly because it was vouched for by such eminent men as Landolt, Ostwald, and Seubert. At the close of the remarks accompanying this table, the three members of the committee expressed the hope that the matter might be clinched by international agreement. The hope was strengthened by the fact that the two other modern tables, those of Clarke and of Richards, differed but slightly from the table presented in Germany. Time has strengthened this hope still farther, for the two subsequent yearly editions of the three tables have steadily tended towards the elimination of earlier differences, until now they are even more alike than they were at first.<sup>2</sup>

On March 30, 1899, having been encouraged by the favorable reception of their work, the German Committee issued, to all important associations interested in chemistry throughout the world, a general invitation to appoint delegates to an International Committee.<sup>3</sup> The number of delegates was not determined, and the outcome was the appointment of 57 men from among the most eminent chemists of 11 nations. As representatives on this International Committee, the American Chemical Society appointed Professors F. W. Clarke, J. W. Mallet, E. W. Morley, T. W. Richards, and E. F. Smith. Shortly afterward the American Academy of Arts and Sciences added Professors Wolcott Gibbs and Ira Remsen to the list of American delegates. Besides these 7 men, the present International Committee contains 15 from Germany, 11 from Austria, 8 from England, 5 from Belgium, 3 each from Switzerland and Italy, 2 from Japan, and 1 each from Holland, Russia, and Sweden. It is much to be regretted that Denmark, France, and Norway have as yet made no appointments.

Having thus received very general support, the German Committee, in October, 1899, decided upon another step. They forwarded to each member of the International Committee a circular letter containing three questions, which were speedily answered by nearly all of the delegates. A literal translation of these questions follows:

"1. Shall  $O = 16$  be fixed as the future standard for the calculation of atomic weights?

<sup>1</sup> Ber. d. chem. Ges., **31**, 2761 (1898).

<sup>2</sup> See J. Am. Chem. Soc., **22**, 78 (1900); also Proc. Am. Acad., **35**, 621 (1900) and Ber. d. chem. Ges., **33**, 1 (1900).

<sup>3</sup> Ber. d. chem. Ges., **31**, 2949 (1898); **33**, 1847 (1900).

"2. Shall the atomic weights be given with so many decimals that the last figure is certain within half a unit, or what other procedure shall be adopted?"

"3. Is it desirable that a smaller committee should be formed, which should undertake the continual revision of the yearly atomic weight table and its publication? In case of agreement upon this point it is proposed that each association shall name a single delegate to this smaller committee."

The 49 answers to these questions are highly interesting.<sup>1</sup> As regards the first question, only 7 chemists (1 American and 6 Germans), were decidedly in favor of retaining hydrogen as the standard, while 40 were decidedly of the opposite opinion. Two were willing to accept either or both standards of reference. In spite of the fact that men as eminent as Professors Mallet, Volhard, Winkler, and Wislicenus are in the minority, the majority is so overwhelming that we must look upon this point as settled for a long time. Even if the probable delegates from the unrepresented countries should all vote in the negative, the majority must remain in favor of  $O = 16.000$ . Thus the new term "international atomic weight" is perfectly clear and unequivocal in its meaning as to the standard of reference, and an important step has been taken.

It may not be irrelevant here to enumerate the advantages and disadvantages of this international standard. In the first place, it is evident that the question is a practical one, not a theoretical one. If Prout's ancient hypothesis seemed at all probable, there would indeed be a strong reason for assuming hydrogen as unity; but Prout's hypothesis cannot now claim serious consideration, at any rate in its original form. No other theoretical reason for calling hydrogen exactly 1.000 is known to me. What, then, are the relative *practical* advantages to be gained by taking hydrogen or oxygen as the standard? In the first place, the precise quantitative analysis of compounds containing hydrogen is a very difficult matter, and water is the only one which has been adequately studied. Hence nearly all atomic weights must be referred to hydrogen through the medium of oxygen; and if the ratio  $H:O$  is found to be even a little in error, all other values must be recalculated. Morley's work on this ratio is indeed magnificent, and it is not likely that his accuracy can be surpassed for a long time; nevertheless the principle still remains. Oxygen on the other hand has been directly compared with many metals, as well as with potassic chloride and similar salts obtainable from the chlorates and their analogues. Hence from

<sup>1</sup> Ber. d. chem. Ges., **33**, 1853 (1900). The answers are published in full.

the point of view of directness of comparison, oxygen is to be preferred. Silver might be even better, as Erdmann and Volhard point out in their replies to the circular letter; but the question does not concern the starting of an entirely new system, but rather the choice between the two old ones.

Another point to be considered is the effect of the decision upon the data contained in the past literature of chemistry. Any change which tends to confuse the understanding of the work of the past would be indeed a grievous one; and a change to  $O = 15.879$  could not but have this effect. Little or nothing has been written with the assumption of this standard, while a great bulk has been written with the assumption  $O = 16$ . The confusion caused by the inaccurate value  $O = 15.96$  is quite bad enough, without the introduction of a new stumbling block. Moreover, in the gas-constant and a multitude of other physico-chemical constants the value  $O = 16$  enters, and a change in this standard would complicate the use of a great mass of valuable literature of this kind.

Another, although somewhat trivial, reason why oxygen should be taken as 16 is because in that case a somewhat larger proportion of the atomic weights approximate whole numbers than would be the case otherwise.

The chief objection to the proposed standard is a pedagogical one. It is claimed that confusion is caused in the mind of the student by the use of the number 1.0075.<sup>1</sup> The German Committee points out in its last report that this difficulty may be avoided by giving the elementary student only the round numbers (which suffice amply for his purpose), accompanied by the statement that these are rough approximations. There is obviously another way of avoiding the confusion, and that is by doing away with hydrogen as a standard of specific gravity. The difficulty of preparing this gas in a pure state, and its great lightness are arguments against it, in any case. Moreover, in my experience the simplicity of the relationship between the specific gravity referred to hydrogen and the molecular weight is quite as likely to be a stumbling block as an assistance. Many a beginner learns by heart the statement that the specific gravity is twice the molecular weight; for he does not pause to think about it and see that he has inverted the ratio. If on the other hand the specific gravity of oxygen is taken as the standard, the adverse arguments disappear, and even a dull student can hardly forget the reason why the specific gravity of the gas X referred to oxygen must be multiplied by 32 to give the molec-

<sup>1</sup> Much has been written upon both sides of this question. Besides the articles already referred to, many references may be found in two papers by Küster and Brauner [*Ztschr. anorg. Chem.*, **14**, 251 and 257 (1897)].

ular weight. For several years I have used this method with large classes, and find that it gives no trouble. The only data needing recalculation are the specific gravities of the gases, and that is a simple matter. It seems to me, by the way, that the use of 2 instead of R in physico-chemical formulae has the same pedagogic fault of obscuring the source and nature of the symbol, as this use of 2 for the molecular weight of hydrogen.

The answers to the second international question, which seeks to determine the number of decimal places to be given, support the German Committee in its position with a majority almost as overwhelming as in the case of the first question. The minority of 8 consists of 3 Americans, 3 Germans, and 2 Japanese, all the others desiring to omit all figures which are not certain to within half a unit. The committee in summing up the opinion upon this subject states that its desire is to propose a table for common use, and that the minority, which desires the retention of one uncertain decimal place, has rather had in mind the requirements of work of the greatest precision. Undoubtedly the curtailed table will answer for most purposes, but it seems to me that the nature of the decimal notation causes an unfortunate incompleteness in it. Although in the face of so great a majority, this matter, like the other, must be considered as settled, I am tempted to call attention to this incompleteness in relation to numerical data of all kinds.

Let us consider a concrete example—the case of nitrogen. Few would be willing to contend that the last figure in the number 14.04 is certain. Let us assume, for the sake of argument, that this atomic weight may really be as low as 14.034 or as high as 14.046. According, then, to the rule which has just been adopted by the International Committee, the figure 4 should be omitted, and nitrogen should be called 14.0. Such an omission causes an error far greater than the uncertainty which leads to the dropping of the figure. The uncertainty named above is only 0.04 per cent, but the minimum error in the value 14.0 is 0.24 per cent, if the lower value given above is supposed to be the lowest possible. Clearly one must either record uncertain figures, or else omit figures which have a real significance. The dropping of a decimal place at once reduces tenfold the power of a number to express slight changes of value; but numerical results may have any degree of accuracy, and cannot be placed strictly in classes separated by gaps so wide. For this reason it is a well-known practice in scientific calculation to retain during the calculation one uncertain figure, while a final result is

often relieved of this uncertain figure. According to this rule, the table of atomic weights should always give an uncertain figure in each value, for atomic weights are simply data for further calculation. If this is done, the user has all the truth, and may reject as much of it as his occasion permits. Such a table of atomic weights seems to me to be the best, because it is capable of fulfilling all uses.

Quite another point of view should be adopted in making a table solely for common use. Here we are concerned not with the number of exact figures which may have been determined by Stas, but rather with those figures which will have an influence upon the work in hand. Usually the error in such a value is important not on account of its absolute magnitude, but rather on account of its relation to the value itself. In short, the percentage error is that which ought to be considered in constructing a table of atomic weights for common use. A majority of chemists would probably decide that a table in which the numbers were within 0.1 per cent of their true values would serve all ordinary purposes. Most common methods are not able to attain as great a degree of accuracy even as this, but the admission of a wider range of inaccuracy in a table of atomic weights might by summation cause an appreciable error.

Silver might be called 108.0, chlorine, 35.5, bromine, 80.0, iodine, 126.9, potassium, 39.2, sulphur, 32.1, and lead 207.0 without seriously affecting the results of most quantitative work, and indeed everyone frequently uses such approximate values. Even in this approximate table hydrogen should be 1.008, and not 1.01, however, if the percentage rule is to be followed.

The last question asked by the German Committee, suggesting the appointment of a small standing committee, was answered affirmatively by every one. The original plan of having a representative from each society would evidently result in the formation of an unwieldy body, hence the German Committee has wisely concluded that a small number, perhaps three, should be elected from among those who have had especial experience in the matter of atomic weights.

The matter is by no means finished. The German Committee asks anyone who has anything new to say upon the questions under consideration to send a brief statement of his views to Professor Landolt before Nov. 15th, and some new ideas may have been advanced in the discussion in Paris at the end of July. The balloting for the smaller International Committee is now taking place. The German Chemical Society, and the members of its committee, are greatly to be con-



gratulated on the success of the undertaking. Much progress has already been made in a matter important not only in itself, but also in its relation to the growing international scientific understanding.

MT. DESERT, MAINE,  
August 6, 1900.

THEODORE WILLIAM RICHARDS.

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## REVIEWS.

COMMERCIAL ORGANIC ANALYSIS. BY ALFRED H. ALLEN, F.I.C., F.C.S. Third edition, illustrated, with revisions and addenda by the author and HENRY LEFFMANN, M.A., M.D. Volume I: Introduction, Alcohols, Neutral Alcoholic Derivatives, Sugars, Starch and Its Isomers, Vegetable Acids, etc. Philadelphia: P. Blakiston's Son & Co. 1898. pp. 557. Price \$4.50.

Volume II, Part II: Hydrocarbons, Petroleum, and Coal Tar Products, Asphalt, Phenols and Creosotes, etc. 1900. pp. 330. Price, \$3.50.

This work has been so long a standard one, and is so extremely useful for the subjects of which it treats, that all chemists will welcome a new edition. While the appearance of an unauthorized reprint of an older edition may be considered as an excuse for haste in getting out the first volume, it is unfortunate that time could not have been taken for a more thorough revision. In a number of cases erroneous statements, which might have been easily corrected by reference to recent standard works on organic chemistry, have been allowed to stand. Thus, on p. 232, an old and incorrect equation is given for the formation of chloroform from alcohol. On p. 243 sugars are defined as polyatomic alcohols and so many misleading and erroneous statements are included in the classification which follows as to make that portion of the book almost useless. The practical treatment of the analysis of sugars, which is, after all, much more vital to the usefulness of the book, is more satisfactory. The material which is given could have been made much more easily available, however, by careful digestion and rewriting in such a manner as to incorporate the new portions with the old.

The revision of the second part of the second volume has been more complete and a large amount of new and useful matter has been added. The reactions upon asphalt and upon phenols have, especially, been largely increased. Some errors are, of course, to be found, but these are, mostly, of such a nature as not to impair the book seriously for the practical purpose for which it is intended. The claim of the preface that the nomenclature of the Geneva convention has been applied is not justified by an examination of the text. In the classification on p. 18, ethyl, propyl, and similar radicals are

spoken of as hydrocarbons. The erroneous statement that hydrogen is found in natural gas is given and illustrates the difficulty of correcting an error which has found its way into text-books.

While criticizing minor defects it would be unjust not to emphasize the fact that the general excellence of the work is such as to make it almost indispensable to any chemist working in this field.

W. A. N.

THE MANUFACTURE OF VARNISHES, OIL CRUSHING, REFINING AND BOILING, AND KINDRED INDUSTRIES. Translated from the French of ACH. LIVACHE, Ingénieur Civil des Mines, greatly extended and adapted to English practice, with numerous original recipes, by JOHN GEDDES MCINTOSH, Lecturer and Demonstrator on the Manufacture of Painters' Oils, Colors, and Varnishes, Regent Street Polytechnic. London: Scott, Greenwood & Co. 1899. New York: D. Van Nostrand Co. pp. vii + 403. Price, \$5.00.

This book includes in its general scope a description of the sources and character of the raw materials used in making varnishes, together with some account of methods of manufacture and of processes for the qualitative and quantitative examination of the various substances involved.

From the chemical standpoint the book leaves much to be desired. Many erroneous statements are made which indicate ignorance or carelessness. Thus, on p. 88, a statement is given which implies that picrate of ammonia is formed by neutralizing picric acid with soda. On p. 105, amyl acetate is said to be formed by heating amyl iodide to  $120^{\circ}$  C. with silver nitrate. Occasionally antiquated names or even antiquated formulæ are used; as sulphovinic acid for ethylsulphuric acid or the acid ethyl ester of sulphuric acid, and  $\text{EtO}_2\text{Na}$  for sodium ethylate.

The accounts of raw materials and of processes of manufacture are fairly satisfactory. The directions for analysis are, however, often so concise that a chemist unacquainted with the methods used with this class of materials would find some difficulty in following them.

W. A. N.

# AMERICAN CHEMICAL JOURNAL

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## THE MOLECULAR WEIGHT OF ALUMINIUM COMPOUNDS.

BY ELMER P. KOHLER.

The molecular weight of aluminium compounds has been the subject of investigations by Deville and Troost,<sup>1</sup> Odling and Buckton,<sup>2</sup> V. Meyer and C. Meyer,<sup>3</sup> Nilson and Pettersson,<sup>4</sup> Friedel and Crafts,<sup>5</sup> Roux and Louise,<sup>6</sup> Combes,<sup>7</sup> and Werner and Schmujlow.<sup>8</sup> All of the earlier results, obtained by applying vapor-density methods to aluminium halides, lead to the general formula  $Al_2X_6$  for these salts. All the later results—obtained partly by vapor-density and partly by newer methods—lead to the general formula  $AlX_3$  for all classes of aluminium compounds. The last two investigations, in particular, have appeared so conclusive that the double formulas have been more or less reluctantly abandoned. Combes determined the vapor-density of aluminium acetylacetone and obtained results that agree perfectly with the formula  $Al(C_5H_7O_2)_3$ , showing that in compounds of this type aluminium is unquestionably trivalent. Werner and Schmujlow de-

<sup>1</sup> Ann. chim. phys. [3], **58**, 257.

<sup>2</sup> Phil. Mag. [4], **29**, 316.

<sup>3</sup> Ber. d. chem. Ges., **12**, 1199.

<sup>4</sup> Ztschr. phys. Chem., **1**, 456.

<sup>5</sup> Compt. rend., **106**, 73; **106**, 602; **107**, 600.

<sup>6</sup> *Ibid.*, **106**, 1764.

<sup>7</sup> *Ibid.*, **108**, 405.

<sup>8</sup> Ztschr. anorg. Chem., **15**, 24.

terminated the molecular weight of aluminium chloride by the boiling-point method, using pyridine as solvent. Their results agree closely with the formula  $\text{AlCl}_3$ .

The investigation described in this paper was undertaken as a result of some observations made while studying the mechanism of organic reactions, that are induced by aluminium halides. The aim was the determination of the molecular weight of aluminium halides, as well as that of their addition- and reaction-products, as nearly as possible under the same conditions as those under which they are used and formed in organic reactions; namely, dissolved in some low-boiling, indifferent medium.

The substances studied were:

I. Organic compounds like aluminium acetylacetone.

II. Aluminium halides.

III. Compounds formed by the addition of aluminium halides to a number of different classes of organic and inorganic compounds.

Nearly all the determinations were made by the boiling-point method, with carbon disulphide as solvent; but at the end of the paper some experiments are described in which nitrobenzene was used as solvent for determinations by the freezing-point method. These were made to determine the behavior of the addition-products, above referred to, in the presence of a large excess of one of the components. They show the relation between the results described in this paper and those obtained by Werner and Schmuylow.

#### I. ORGANIC ALUMINIUM COMPOUNDS.

##### *Aluminium Acetylacetone.*

Solvent: Carbon disulphide.  $K = 2,370$ .

	Solvent. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
1	39.4195	1.2340	0.194	329
2	"	1.7848	0.330	326
3	"	2.3458	0.425	331

Mean, 328

Calculated for  $\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$ , 324.3

*Aluminium Acetoacetic Ester.*Solvent : Carbon disulphide.  $K = 2,370$ .

	Solvent. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
1	40.1505	1.5400	0.220	413
2	"	2.1825	0.306	421
3	"	2.8050	0.396	418

Mean, 417

Calculated for  $\text{Al}(\text{C}_6\text{H}_9\text{O}_3)_3$ , 414.4

These determinations presented no difficulties, and the results, as expected, fully confirm those of Combes.

## II. ALUMINIUM HALIDES.

Aluminium chloride is insoluble in carbon disulphide, hence its molecular weight could not be determined directly. An indirect determination is given under the addition-products.

Aluminium bromide was made by Mallet's method,<sup>1</sup> from pure bromine and metallic aluminium. To avoid the troublesome distillations, necessary to free it from bromides of carbon, silicon, and iron, the following method of purification was adopted : A piece of Jena-glass tubing 3 meters long was constricted at three points, and bent, at the constrictions, into a flattened W. One of the ends was drawn into a capillary and connected with a phosphorus pentoxide drying-tube which, in turn, was connected with a pump. Aluminium wire that had been heated to a low red heat in a current of hydrogen was placed in the limb next to the other end, that connected with the retort in which the bromide had been prepared, and the latter distilled into the tube. This end of the tube was then sealed off. The limb holding the bromide and wire was wrapped with thin asbestos paper and placed in a furnace in such a position that the second limb served as a reflux condenser. The bromide was boiled until colorless, when the other end of the tube was sealed off, the position of the tube changed, and the bromide distilled from the first into the second limb. The first limb was then sealed off at the constriction, the position of the tube changed; and the distillation repeated, etc.

<sup>1</sup> Trans. Roy. Soc. (1880), 1903; and This JOURNAL, 3, 77.

The second distillation left a slight residue of oxybromide ; the third no residue at all. The bromide was thus obtained sealed up in the fourth limb. To get it into convenient form for use, it was melted into a layer of uniform thickness throughout the length of the tube. By hitting the tube sharply with a block of wood the layer could be readily broken up into lumps of any desired size. In this way there is no difficulty either in preparing or manipulating the bromide.

The principal difficulty met with in this part of the work consisted in getting and keeping carbon disulphide sufficiently free from water. After a most careful purification it was repeatedly distilled from phosphorus pentoxide ; but though used immediately after distillation, enough water was invariably present to cause errors of from 50 to 100 in the molecular weight. The difficulty which has been experienced by others<sup>1</sup> working with such sensitive substances, is due to the adsorption of water by the apparatus. To remove this water, the weighed molecular-weight apparatus was filled with dry carbon disulphide, and a considerable quantity of the latter distilled off, the vapor sweeping freely through the condenser. The condenser was then capped with phosphorus pentoxide tubes that were ground on, the apparatus closed with a ground glass stopper, and weighed with the thermometer in place.

Pure dry carbon disulphide dissolves aluminium bromide without any indication of chemical action. The solution is clear and colorless ; its boiling-point remains constant during protracted boiling ; and, if the disulphide is allowed to evaporate at ordinary temperatures, the pure bromide crystallizes out in large, lustrous rhombohedra. These are far less sensitive to atmospheric moisture than the lumps of the fused salt. An analysis of the crystals gave 10.02 per cent aluminium and 89.72 per cent bromine, instead of the calculated 10.15 per cent aluminium and 89.85 per cent bromine.

*Molecular Weight of Aluminium Bromide.*

Solvent : Carbon disulphide.  $K = 2,370$ .

<sup>1</sup> Rosenheim and Woge : Ztschr. anorg. Chem., 15, 283.

	Solvent. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
1	40.1510	0.6110	0.067	539
2	"	1.3660	0.149	542
3	"	2.2895	0.250	540
4	"	3.1000	0.340	538
5	"	3.7410	0.405	545
6	"	4.3840	0.479	540

Mean, 540.6

Calculated for  $\text{Al}_2\text{Br}_6$ , 534

### Aluminium Iodide.

The iodide was prepared by the method of Gustavson,<sup>1</sup> and purified in exactly the same way as the bromide.

Solvent: Carbon disulphide.  $K = 2,370$ .

	Solvent. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
1	40.4550	1.0120	0.072	824
2	"	1.5175	0.110	808
3	"	2.2380	0.160	819
4	"	3.1080	0.222	822
5	"	4.3200	0.310	826

Mean, 822.25

Calculated for  $\text{Al}_2\text{I}_6$ , 815.30

### III. ADDITION-PRODUCTS.

Aluminium bromide, like aluminium chloride, combines directly with acid chlorides, ketones, esters, nitro compounds, and tertiary amines. The compounds obtained with the bromide are invariably more easily soluble in carbon disulphide than those obtained with the chloride. It is, therefore, easier to get them in a form in which it is possible to use them for molecular weight work. They are, at best, extremely difficult to manipulate, and only very few gave satisfactory results. With these, however, it was possible to prove that for the purpose of this investigation it is not at all necessary to isolate the substances. They can just as well be made in the apparatus in which their molecular weight is to be determined.

<sup>1</sup> Ann. Chem. (Liebig), 172, 173.

*Benzene Sulphonchloride and Aluminium Bromide.*

Slightly more than 2 molecules of pure benzene sulphonchloride were added to 1 molecule of aluminium bromide dissolved in a large amount of carbon disulphide. The flask was closed with a phosphorus pentoxide tube and the disulphide allowed to evaporate slowly through the tube. In the course of a week the product began to separate in large, colorless tables. The solution was removed in a current of dry air, the crystals washed with dry disulphide, dried in a current of dry air, and used without further purification. A halogen determination gave the following results :

- I. 0.3245 gram substance gave 0.5152 gram silver halide.  
 II. 0.4105 gram substance gave 0.6530 gram silver halide.

Cl, Br	Calculated for (AlBr <sub>3</sub> .C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> Cl) <sub>x</sub> .	Found.	
		I.	II.
	62.07	61.8	61.9

*Molecular Weight of (AlBr<sub>3</sub>.C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>Cl)<sub>x</sub>.*

Solvent : Carbon disulphide.  $K = 2,370$ .

	Solvent. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
1	40.1110	1.0030	0.086	899
2	"	1.9230	0.128	887
3	"	3.1255	0.210	879
4	"	3.7110	0.244	898
Mean,				890.75
Calculated for Al <sub>2</sub> Br <sub>6</sub> .2C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> Cl,				887.08

*Nitrobenzene and Aluminium Bromide.*

Gatterman<sup>1</sup> found that aluminium chloride combines with nitrobenzene to form a crystalline addition-product of the composition AlCl<sub>3</sub>.C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>. The corresponding aluminium bromide compound crystallizes well, at low temperatures, forming large yellow prisms considerably less sensitive to atmospheric moisture than the analogous addition-products with acid chlorides. The substance was washed with dry carbon disulphide and dried in a current of air.

<sup>1</sup> Ber. d. chem. Ges., 12, 2719.



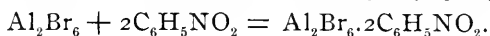
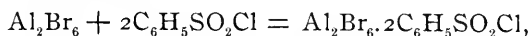
Molecular Weight of  $(AlBr_3 \cdot C_6H_5NO_2)_x$ .Solvent : Carbon disulphide.  $K = 2,370$ .

	Solvent. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
1	40.2020	0.8510	0.064	784
2	"	1.8200	0.135	794
3	"	2.3840	0.178	789
4	"	2.9630	0.220	794

Mean, 790.25

Calculated for  $Al_2Br_6 \cdot 2C_6H_5NO_2$ , 780.14

According to these results, 1 molecule of aluminium bromide combines with 2 molecules of other substances to form 1 molecule of product :



If these equations are correct, then the addition of sulphonchloride or nitro compound to a solution of aluminium bromide of known boiling-point should not affect the boiling-point so long as the bromide is in excess ; while the addition of the bromide to a solution of benzene sulphonchloride or nitrobenzene should immediately lower the boiling-point, and the lowering should be proportional to the gram-molecular amounts of bromide added. The experimental results are as follows :

*Effect of Adding Benzene Sulphonchloride to a Solution of Aluminium Bromide.*Solvent : Carbon disulphide.  $K = 2,370$ .

	Solvent. Grams.	Bromide. Grams.	Sulphon- chloride. Grams.	Boiling- point.	Change in boiling-point.
1	39.7150	....	....	2.572	....
2	"	1.7730	....	2.770	0.198
3	"	"	0.2335	2.770	0.000
4	"	"	0.6980	2.770	0.000
5	"	"	1.1840	2.810	0.040

The weight of sulphonchloride equivalent to 1.7730 grams aluminium bromide is 1.1749 grams ; the amount added is 1.1840 grams ; the elevation of the boiling-point calculated

for the difference, assuming—what is only approximately true—that the constant for the solution is the same as that for the pure solvent, is 0.045; the elevation found is 0.040.

*Effect of Adding Aluminium Bromide to a Solution of Benzene Sulphonchloride.*

	Solvent. Grams.	Sulphon- chloride. Grams.	Bromide. Grams.	Boiling- point.	Change in boiling-point.
1	41.8860	....	....	2.590	....
2	"	2.5150	....	3.394	+0.804
3	"	"	0.5050	3.342	—0.052
4	"	"	1.3800	3.247	—0.142
5	"	"	2.5950	3.118	—0.275

The molecular weight of aluminum bromide calculated from these lowerings, assuming  $K = 2,370$  is as follows :

	Solvent. Grams.	Bromide. Grams.	Lowering of boiling-point.	Molecular weight.
1	41.8860	0.5050	0.052	560
2	"	1.3800	0.142	548
3	"	2.5950	0.275	536
		Calculated for $Al_2Br_6$ ,		534

No better proof of the formula  $Al_2Br_6$  seems possible. No other assumption would explain these results. It will be observed that the error introduced by the presence of the sulphonchloride is small in comparison with the normal error of these determinations, which is unavoidably large, partly owing to the sensitiveness of the substances and partly to their great molecular weight. Knowing that aluminium chloride combines with nitrobenzene to form a compound  $(AlCl_3 \cdot C_6H_5NO_2)_x$ , it is possible to determine whether the formula of the chloride is analogous to that of the bromide or not.

*Aluminium Chloride and Nitrobenzene.*

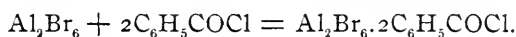
Solvent : Carbon disulphide.  $K = 2,370$ .

	Solvent. Grams.	Nitrobenzene. Grams.	Chloride. Grams.	Lowering of boiling-point.	Molecular weight.
1	40.2250	2.1310	0.8250	0.170	284
2	"	"	1.4355	0.308	275
3	"	"	2.0310	0.444	270
Mean,					276.33
Calculated for $Al_2Cl_6$ ,					266.9

The facts established up to this point supply an elegant method for determining what happens when an aluminium halide is brought in contact with a given substance in an indifferent medium. It is sufficient, for this purpose, to prepare a solution of aluminium bromide, of known concentration and boiling-point, to add to this successive portions of the substance under investigation, until it is present in excess, and then add a fresh portion of aluminium bromide. The thermometer readings after each addition of material, give an accurate account of what goes on in the solution. The following results were obtained in this way :

*Aluminium Bromide and Benzoyl Chloride.*

The calculations are based on the equation

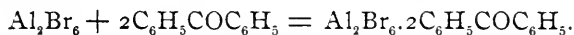


Solvent : Carbon disulphide.  $K = 2,370$ .

	Solvent. Grams.	Bromide. Grams.	Chloride. Grams.	Change in boiling-point.	Calculated change in boiling-point.
1	38.1500	1.7140	....	+0.020	+0.0215
2	"	"	0.3370	0.000	0.000
3	"	"	0.9460	0.000	0.000
4	"	"	1.2380	+0.128	+0.130
5	"	2.2670	"	-0.053	-0.054

*Aluminium Bromide and Benzophenone.*

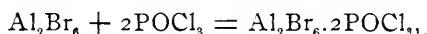
The calculations are based on the equation,



	Solvent. Grams.	Bromide. Grams.	Ketone. Grams.	Change in boiling-point.	Calculated change in boiling-point.
1	40.1510	1.1010	....	+0.118	+0.121
2	"	"	0.4117	0.000	0.000
3	"	"	1.3290	+0.211	+0.213
4	"	1.6120	"	-0.054	-0.057

*Aluminium Bromide and Phosphorus Oxychloride.*

The calculations are based on the equation,



	Solvent. Grams.	Bromide. Grams.	Oxychloride. Grams.	Change in boiling-point.	Calculated change in boiling-point.
1	40.2150	1.3520	....	+0.147	+0.150
2	"	"	0.6772	0.000	0.000
3	"	"	1.2282	0.172	+0.173
4	"	1.8070	"	-0.047	-0.050

*Aluminium Bromide and Dibrombenzene (p).*

The Friedel and Crafts reaction is not applicable to di-halogen compounds. The experiment was made to determine whether this is due to a combination of the halogen compound with the aluminium halide. The results show that this is not the case. The calculations are based on the assumption that both substances are present unchanged :

	Solvent. Grams.	Bromide. Grams.	Dibrom- benzene. Grams.	Rise in boiling-point.	Molecular weight.
1	40.6650	1.7000	....	0.186	533
2	"	"	0.5860	0.140	244
3	"	"	1.4400	0.340	246
4	"	"	2.2040	0.540	240
5	"	2.8050	"	0.120	540
			Calculated for $\text{Al}_2\text{Br}_6$ ,		534
			Calculated for $\text{C}_6\text{H}_4\text{Br}_2$		236

Of other substances examined, acetophenone, benzene sulphonacetone, and ethyl benzoate, form addition-products with aluminium halides, and behave like benzophenone. Benzene and naphthalene give results like those of dibrombenzene, but they slowly react to form insoluble compounds. Pyridine and quinoline form crystalline addition-products insoluble in carbon disulphide.

The results thus far given show conclusively that in an indifferent medium the aluminium halides form addition-products that are not measurably dissociated. The results are quite different when a large excess of one of the components is present. It was shown, above, that in carbon disulphide aluminium bromide combines with nitrobenzene to form a compound of the formula  $\text{Al}_2\text{Br}_6 \cdot 2\text{C}_6\text{H}_5\text{NO}_2$ . If this compound, or aluminium bromide itself, is dissolved in nitrobenzene and the lowering of the freezing-point of the latter measured, the result leads to a much simpler formula.

*Aluminium Bromide in Nitrobenzene.*

$$K = 7,070.$$

	Nitrobenzene. Grams.	Bromide. Grams.	Lowering of freezing-point.	Molecular weight.
1	15.2470	1.2530	2.11	275.5
2	"	1.9040	3.20	276.0
3	"	2.4250	4.08	277.0

Mean, 276.17

Calculated for  $\text{AlBr}_3$ , 267

*Aluminium Chloride in Nitrobenzene.*

$$K = 7,070.$$

	Nitrobenzene. Grams.	Chloride. Grams.	Lowering of freezing-point.	Molecular weight.
1	19.7640	0.1893	0.520	130.4
2	"	0.5953	1.675	127.5
3	"	0.8923	2.500	131.0

Mean, 129.63

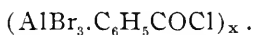
Calculated for  $\text{AlCl}_3$ , 133.4

The results are exactly like those obtained in pyridine solution. As a mean of six determinations of the molecular weight of aluminium chloride in pyridine, Werner and Schmujlow obtained the value 129.6, and Werner concludes that  $\text{AlCl}_3$  is the only formula permissible. The conclusion is not justified. Pyridine combines with aluminium chloride to form a well crystallized compound, and there is no experimental evidence that molecular weight determinations, made in solvents that combine with the substance under investigation, are trustworthy. In aqueous solutions they are not, and my results show that they are equally unreliable in this case. Between the results in carbon disulphide and those in nitrobenzene or pyridine, it is easy to decide by the aid of the following considerations: In the absence of any solvent benzoyl chloride combines with aluminium bromide to form a well crystallized compound which, as shown by analysis, has the composition  $(\text{AlBr}_3 \cdot \text{C}_6\text{H}_5\text{COCl})_x$ . The molecular weight must, therefore, correspond to some multi-

ple of this formula. The determination in carbon disulphide gave a value corresponding to the double formula



—a possible value. The determination in nitrobenzene gives an impossible value:



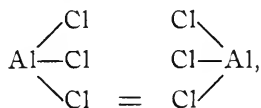
Solvent: Nitrobenzene.  $K = 7,070$ .

	Solvent. Grams.	Substance. Grams.	Lowering of freezing-point.	Molecular weight.
1	20.2500	0.5820	0.424	371
2	"	1.0105	0.952	370
3	"	1.8200	1.710	371

Calculated for  $(\text{AlBr}_3 \cdot \text{C}_6\text{H}_5\text{COCl})_x$ ,  $(407.5)_x$ .

It is evident from these results that nearly all the values for inorganic salts obtained by Werner and his pupils will need redetermination, since they purposely selected solvents that combine with salts and in many cases proved combination by isolating the products. The same is true of the determinations made by Lespeau<sup>1</sup> in ether, and those by Rosenheim and Woge<sup>2</sup> in pyridine.

The principal objections to the double formulas for the aluminium halides have been based on the assumption that these formulas imply quadrivalent aluminium.<sup>3</sup> To avoid this Traube<sup>4</sup> assumed that these salts are derived from an hexavalent complex of two aluminium atoms,  $[\text{Al} \equiv \text{Al}]^{\text{VI}}$ . Neither of these assumptions is necessary. The aluminium halides behave like typical double halides with the formula  $\overset{\text{III}}{\text{Al}}\text{Cl}_3 \cdot \overset{\text{III}}{\text{Cl}}_3\text{Al}$  or the formula  $(\overset{\text{III}}{\text{Al}}\text{X}_6)\overset{\text{III}}{\text{Al}}$ . Their behavior in nitrobenzene and pyridine, moreover, makes it fairly certain that no double molecules are present in aqueous solution. The hydrous salt that crystallizes out of aqueous solutions is probably  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ . The anhydrous salt is probably



<sup>1</sup> Bull. Soc. Chim. [3], **17**, 934.

<sup>2</sup> Ztschr. anorg. Chem., **15**, 283.

<sup>3</sup> Erdman: Lehrbuch d. anorg. Chem., 587.

<sup>4</sup> Ber. d. chem. Ges., **25**, 1716.

a double halide in harmony with Remsen's law.<sup>1</sup> The formula expresses the molecular weight, the power of direct addition, and the ease with which the substance is dissociated at higher temperatures and in solution. In any case I believe that the matter can be reached by experiment and the work will be continued in this direction and extended to include the compounds of iron.

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## THE HYDROLYSIS OF ACID AMIDES.

BY EMMET REID.

In a previous article<sup>2</sup> I have given the results of a number of experiments on the rate of hydrolysis of the three nitrobenzamides both with acids and with alkalies, and of a number of other amides with hydrochloric acid. In the present work several other amides have been tried with hydrochloric acid, and all the amides available have been hydrolyzed with barium hydrate. It has seemed desirable to obtain additional measurements on some of the amides previously studied.

### *Preparation of Material.*

For the amides previously worked upon, the same preparations have been used.

*o*-Phenoxybenzamide was readily made from *o*-phenoxybenzoic acid obtained from salol. 90 grams salol gave 22 grams *o*-phenoxybenzoic acid, and this with 22 grams phosphorus pentachloride yielded 13 grams of the amide. This required about 5 liters of boiling water for its solution, from which 10 grams of pearly crystals were obtained on cooling. The amide melted at 130° (corr.). The melting-point given in the literature is 128°.5–129° C. *o*-Brombenzamide was prepared from the *o*-brombenzoic acid obtained by extracting with hot water the mixture of brombenzoic acids resulting from the oxidation of liquid bromtoluene with potassium permanganate. The amide melted at 155°.6 (corr.), the melting-point given

<sup>1</sup> This formula is essentially the same as that used by Remsen (This JOURNAL, 11, 316) to account for the peculiar results obtained in the determination of the vapor-density of aluminium chloride.

<sup>2</sup> This JOURNAL, 21, 284.

in the literature being  $155^{\circ}$ – $156^{\circ}$ . *p*-Methoxybenzamide was made from anisic acid prepared by oxidizing *p*-methoxytoluene obtained according to Alleman's directions.<sup>1</sup>

*p*-Ethoxybenzamide was made from *p*-ethoxybenzoic acid similarly prepared.

*o*-Dimethylamidobenzamide was made by heating in a sealed tube *o*-amidobenzamide with methyl iodide. These three amides were identified by their melting-points but, I am sorry to say, the record has been lost.

### *Experiments with Hydrochloric Acid.*

These form a continuation of the work already published, the methods of work being the same. That is, the required amount of amide was weighed out in a light weighing-bottle and dropped into a flask containing 600 cc. of hydrochloric acid of the proper strength. This flask had been for some time in a vigorously boiling water-bath. At intervals of thirty minutes samples were taken out, diluted with a known amount of water, cooled and measured, and the ammonia present determined by distilling with magnesium hydroxide into a standard acid. *o*-Phenoxybenzamide gave much trouble on account of its slight solubility, even in hot water. For this reason only half the usual concentration could be used. This increased the analytical difficulties. The second series is better than the first.

The columns of figures correspond to those in the previous article. The first gives time in minutes; the second the number of cubic centimeters of standard acid neutralized by the ammonia distilled from the sample. The third is the volume of the sample, while the fourth is the number of cubic centimeters of standard acid that would have been neutralized by the ammonia had all the amide in the sample been decomposed. The next is derived from these and gives the percentage of amide hydrolyzed. *A* is the concentration of the acid and *B* that of the amide. The eighth column contains the value of  $K = \frac{2.3025}{(A-B)t} \cdot \log \frac{(A-x)B}{(B-x)A}$ . The last column

<sup>1</sup> Dissertation, Johns Hopkins University, 1897, p. 8.



gives the same value corrected for the expansion of water from the room temperature at which the titrations and other measurements were made to the temperature of boiling water. This rise in temperature decreases the factor  $A-B$  by about 4 per cent, and hence increases the value of  $K$  by the same amount. At the same time a correction has been applied for the variation of the boiling-point due to the variation of barometric pressure. In this the temperature curve found to hold for *m*-nitrobenzamide with caustic soda is assumed to hold. As the differences in temperature are only several tenths of a degree, at most, and the correction is small this seems allowable. In a few of the experiments this temperature correction is not applied owing to lack of data.

### Results.

#### SERIES I.

HCl =  $A = 0.5646$ ,  $B = 0.02013$  N,  $A-B = 0.5445$ ,  $A/B = 28.05$ . B. p. water  $99^{\circ}.85$  C.

*o*-Phenoxybenzamide, 2.379 Grams.

<i>t</i> .	Changed.	Volume of sample.	Equiva- lent of sample.	Per cent changed.	$A-x$ .	$B-x$ .	$K$ .	$K$ (cor.).
30	1.11	65.5	9.20	12.1	2793	87.9	0.00763	(0.00700)
60	1.72	64.2	9.01	19.9	2785	80.1	0.00657	0.00688
90	2.15	64.9	9.11	23.6	2781	76.4	0.00532	0.00557
120	2.42	54.0	7.58	31.9	2773	68.1	0.00570	0.00597
150	2.68	56.3	7.81	34.3	2771	65.7	0.00496	0.00518
180	3.80	67.1	9.42	40.4	2765	59.6	0.00513	0.00537
210	2.79	46.0	6.46	43.2	2762	56.8	0.00481	0.00503
240	6.60	94.7	13.30	49.7	2755	50.3	0.00512	0.00536

## SERIES II.

$\text{HCl} = A = 0.5631$ ,  $B = 0.02013$ ,  $A - B = 0.5430$ ,  $A/B = 27.97$ . Temp.  $99^{\circ}.74$  C.

*o*-Phenoxybenzamide, 2.379 Grams.

<i>t</i> .	Changed.	Volume of sample.	Equiv- alent of sample.	Per cent changed <i>x</i> .	$A - x$ .	$B - x$ .	<i>K</i> .	<i>K</i> (cor.).
30	0.80	66.3	9.31	8.6	2789	91.4	0.00534	0.00562
60	1.52	64.6	9.07	16.7	2781	83.3	0.00543	0.00572
90	2.06	65.1	9.14	22.5	2775	77.5	0.00505	0.00532
120	3.02	70.4	9.89	30.5	2767	69.5	0.00542	0.00570
150	3.92	76.3	10.71	36.6	2760	63.4	0.00540	0.00568
180	4.80	83.8	11.77	40.8	2756	59.2	0.00522	0.00549
210	5.24	77.1	10.83	48.4	2749	51.6	0.00565	0.00595
240	5.96	80.2	11.26	52.9	2744	47.1	0.00563	0.00593

$B = 0.04081$ ,  $A - B = 0.5223$ ,  $A/B = 12.80$ .

*o*-Dimethylamidobenzamide, 4.008 Grams.

30	0.29	64.1	18.01	1.7	1278	98.3	0.00098	0.00103
60	0.89	73.8	20.73	4.2	1276	95.8	0.00124	0.00130
90	0.90	63.6	17.85	4.9	1275	95.1	0.00098	0.00103
120	1.44	67.5	18.96	7.4	1273	92.6	0.00113	0.00118
150	1.80	66.6	18.71	9.4	1271	90.6	0.00117	0.00123
180	2.31	72.4	20.34	11.1	1269	88.8	0.00117	0.00123
210	2.91	81.7	22.95	12.4	1267	87.6	0.00115	0.00121
240	3.64	91.2	25.61	13.7	1266	86.3	0.00112	0.00118

## SERIES III.

$\text{HCl} = A = 0.5617$ ,  $B = 0.04026$ ,  $A - B = 0.5214$ ,  $A/B = 13.95$ . Temp.  $100^{\circ}.14$  C.

*p*-Methoxybenzamide, 3.033 Grams.

30	3.38	65.9	18.51	18.3	1377	81.7	0.0121	0.0125
60	5.78	59.4	16.68	34.6	1360	65.4	0.0128	0.0132
90	8.43	65.9	18.51	45.5	1350	54.5	0.0123	0.0127
120	11.44	73.1	20.53	55.7	1339	44.3	0.0124	0.0128
150	11.35	63.0	17.70	64.1	1331	35.9	0.0125	0.0129
180	13.91	68.0	19.10	72.8	1322	27.2	0.0133	0.0137
210	20.08	91.2	25.61	78.5	1317	21.5	0.0135	0.0139

## SERIES III (continued).

*p*-Ethoxybenzamide, 3.313 Grams in 500 cc.

<i>t</i> .	Changed.	Vol. of sample.	Equiv. of sample.	Per cent ch'ged, <i>x</i> .	<i>A</i> — <i>x</i> .	<i>B</i> — <i>x</i> .	<i>K</i> .	<i>K</i> (cor.).
30	4.82	67.0	18.82	25.6	1370	74.4	0.0177	0.0183
60	8.15	64.9	18.23	44.7	1350	55.3	0.0179	0.0185
90	9.12	55.8	15.68	58.2	1337	41.8	0.0177	0.0183
120	10.95	56.5	15.88	69.9	1325	30.1	0.0184	0.0190
150	12.80	59.3	16.65	76.8	1318	23.2	0.0180	0.0186
180	15.07	62.8	17.64	85.4	1310	14.6	0.0198	0.0205
210	23.15	95.4	26.80	86.4	1309	13.6	0.0176	0.0182

*m*-Hydroxybenzamide, 2.773 Grams in 500 cc.

30	3.75	63.9	17.95	20.9	1374	79.1	0.0140	0.0145
60	5.51	55.6	15.62	34.6	1360	65.4	0.0128	0.0132
90	7.96	66.5	18.69	42.6	1352	57.4	0.0112	0.0116
120	8.09	57.7	16.21	49.9	1345	50.1	0.0105	0.0109
150	10.55	67.7	19.02	58.1	1337	41.9	0.0106	0.0110
180	9.77	57.8	16.24	60.0	1335	40.0	0.0093	0.0096
210	16.62	94.0	26.41	63.0	1332	37.0	0.0087	0.0090

## SERIES IV.

HCl = *A* = 0.5603, *B* = 0.2013, *A*—*B* = 0.5402, *A*/*B* = 27.83. Temp. 99°.82 C.

*m*-Iodobenzamide, 1.981 Grams in 400 cc.

30	2.01	58.7	8.24	24.4	2759	75.6	0.0167	0.0175
60	4.24	66.8	9.38	45.2	2738	54.8	0.0181	0.0190
90	5.53	67.4	9.47	58.4	2725	41.6	0.0176	0.0185
120	7.12	70.0	9.83	72.4	2711	27.6	0.0195	0.0204
150	6.10	52.2	7.83	77.8	2705	22.2	0.0182	0.0191
180	9.03	73.0	10.25	88.1	2695	11.9	0.0216	0.0227

*p*-Iodobenzamide, 1.981 Grams in 400 cc.

30	1.70	56.4	7.92	21.5	2762	78.5	0.0146	0.0153
60	4.09	69.3	9.73	42.0	2741	58.0	0.0163	0.0171
90	4.81	62.8	8.82	54.5	2729	45.5	0.0158	0.0166
120	4.95	67.0	9.41	63.2	2720	36.8	0.0151	0.0158
150	5.64	55.2	7.75	72.8	2710	27.2	0.0158	0.0166
180	6.81	62.1	8.72	78.1	2705	21.9	0.0153	0.0160

## SERIES V.

HCl =  $A = 0.5408$ ,  $B = 0.04026$ ,  $A - B = 0.5005$ , $A/B = 13.43$ . Temp.  $99^{\circ}.78$  C.*o*-Brombenzamide, 4.816 Grams.

<i>t</i> .	Charged.	Volume of sample.	Equiva- lent of sample.	Per cent charged, <i>x</i> .	<i>A</i> — <i>x</i> .	<i>B</i> — <i>x</i> .	<i>K</i> .	<i>K</i> (cor.).
60	1.12	64.7	17.73	6.3	1337	93.7	0.00101	(0.00212)
165	3.11	80.9	22.17	14.0	1329	86.0	0.00170	0.00178
210	3.45	72.9	19.96	17.3	1326	82.7	0.00168	0.00177
240	3.59	67.5	18.50	19.4	1324	80.6	0.00167	0.00176
270	4.08	69.0	18.91	21.6	1321	78.4	0.00168	0.00176
300	3.91	59.2	16.22	24.1	1319	75.9	0.00172	0.00180
330	5.11	72.2	19.78	25.8	1317	74.2	0.00169	0.00178

## RECAPITULATION.

*Constants of Amides with Hydrochloric Acid—Constant of Benzamide, 0.0217.*

<i>o</i> -Phenoxy- $\frac{1}{2}$ Conc.	<i>o</i> -Phenoxy- $\frac{1}{2}$ Conc.	<i>o</i> -Dimethylamido-	<i>o</i> -Brom-	<i>p</i> -Methoxy-
(0.00799)	0.00562	0.00103	(0.00212)	0.0125
0.00688	0.00572	0.00130	0.00178	0.0132
0.00557	0.00532	0.00103	0.00177	0.0127
0.00597	0.00570	0.00118	0.00176	0.0128
0.00518	0.00568	0.00123	0.00176	0.0129
0.00537	0.00549	0.00123	0.00180	0.0137
0.00503	0.00595	0.00121	0.00178	0.0139
0.00536	0.00593	0.00118	.....	.....
0.00562	0.00568	0.00120	0.00177	0.0131
<i>p</i> -Ethoxy-	<i>m</i> -Hydroxy-	<i>m</i> -Iodo- $\frac{1}{2}$ Conc.	<i>p</i> -Iodo- $\frac{1}{2}$ Conc.	
0.0183	0.0145	0.0175	0.0153	
0.0185	0.0132	0.0190	0.0171	
0.0183	0.0116	0.0185	0.0166	
0.0190	0.0109	0.0204	0.0158	
0.0186	0.0110	0.0191	0.0166	
(0.0205)	0.0096	(0.0227)	0.0160	
0.0182	0.0090	.....	.....	
0.0185	0.0114	0.0189	0.0164	

*Summary of Average Velocities with Hydrochloric Acid.*

All results are multiplied by 10,000 so as to obtain whole numbers, and those quoted from the former article are further increased 4 per cent so as to compare directly with those given above.

*Benzamide, 217.*

<i>o</i> -Cl	33.3	<i>o</i> -Br	17.7	<i>o</i> -I	11.0	....
<i>o</i> -OH	45.4	<i>o</i> -OCH <sub>3</sub>	121.0	<i>o</i> -OC <sub>2</sub> H <sub>5</sub>	97.0	<i>o</i> -OC <sub>6</sub> H <sub>5</sub> 56
<i>o</i> -NO <sub>2</sub>	5.6	( <i>o</i> -NH <sub>2</sub>	17.8)	( <i>o</i> -N(CH <sub>3</sub> ) <sub>2</sub>	12.0	....
<i>o</i> -CH <sub>3</sub>	22.7	....	....	....	....	....
....	....	<i>m</i> -Br	218	<i>m</i> -I	189	
<i>p</i> -Cl	208	<i>p</i> -Br	204	<i>p</i> -I	164	
<i>m</i> -NO <sub>2</sub>	204	<i>m</i> -NH <sub>2</sub>	185	<i>m</i> -CH <sub>3</sub>	201	
<i>p</i> -NO <sub>2</sub>	245	<i>p</i> -NH <sub>2</sub>	198	<i>p</i> -CH <sub>3</sub>	183	
<i>p</i> -OCH <sub>3</sub>	131	<i>p</i> -OC <sub>2</sub> H <sub>5</sub>	185			

*Discussion of Results.*

The results obtained in this work are in line with those already published. Amides having groups in the meta and para positions are hydrolyzed more slowly than benzamide. Para-nitrobenzamide is the only exception to this rule that I have found so far. The retardation is not great, though *p*-methoxybenzamide is surprisingly stable. The results with the halogens are not strictly comparable with the others as, on account of their slight solubility, only half the regular concentration could be used with them. This makes them go something like 10 per cent faster than they would have done at the usual concentration. Among the halogens, iodine retards more than bromine, and bromine more than chlorine, while the halogen has more effect in the para position than in the meta. With all the groups the nature is of more importance than the mere weight, as NH<sub>2</sub> retards more than NO<sub>2</sub> or bromine, and almost as much as iodine, when all are in the para position.

Three additional ortho amides are presented in this article, *o*-phenoxy, *o*-dimethylamido, and *o*-brombenzamide. They simply strengthen the conclusions reached in the former paper, namely, that ortho groups greatly retard the hydrolysis of

benzamide. As seen in the table above, the halogens stand in their proper order. An iodine atom, in the ortho position, retards the hydrolysis 94.9 per cent, a bromine atom 91.9 per cent, and a chlorine atom only 84.6 per cent. The phenoxy group shows itself nearly analogous to the methoxy and ethoxy groups, though all three of them retard far less than hydroxyl. Kellas, in his work on esterification, wrote out the series,



and supposed that they would give analogous results. The values here given show, once more, that  $-\text{OH}$  is no more analogous to  $-\text{OCH}_3$  than the  $\text{H}-$  of formic acid is to the  $\text{CH}_3-$  of acetic. As for the rest, no further remarks are needed except to say that I regret that I have doubts as to the orthoamidobenzamide used in former experiments.

*Hydrolysis of Amides with Barium Hydrate.*

The experiments here given divide themselves, chronologically, into two groups, those included in Series I. to VI., and those that follow, the two being separated by a considerable interval of time. In the last the same preparations of the amides were used as in the first, but different and more carefully calibrated burettes and other apparatus as well as new standard solutions. The method of working was the same as that previously used for orthonitrobenzamide, that is, an Erlenmeyer flask holding about 125 cc., was fitted with a rubber stopper carrying a glass tube about 30 cm. long, bent over at the top and fitting into the stopper of a U-tube. The desired amount of amide was weighed into the dried flask and 75 cc. of the baryta water measured in, the U-tube attached, and more than enough hydrochloric acid put in the U-tube to neutralize the alkali in the flask. The flask was plunged into boiling water and shaken so as to effect the solution of the amide as quickly as possible. At the end of the desired time the flask was taken out and plunged into cold water. By tilting it at the right moment the acid in the U-tube can be made to suck back into the flask in order to stop the reaction and fix the ammonia. The whole contents of the flask was washed into the still, and the ammonia estimated in the usual way. In a series of experiments, by this method, there are

many difficulties in the way of obtaining concordant results. A number of such flasks were always prepared at the same time, and four of them were usually heated in the same bath. As some of the amides, especially the amido, are very soluble in water while others, such as the parabrom- and iodo- and orthophenoxybenzamide are nearly insoluble, requiring several hundred parts of boiling water for their solution, the timing of the reaction is not accurate. Half a minute was allowed on each timing to allow for heating and solution. Sometimes the same amide, in two flasks treated exactly alike, would dissolve more quickly in one than in the other. As the ammonia liberated in the reaction is not held by the hot alkali, there is considerable danger of its escaping if the stopper is not perfectly tight. There is one advantage, and that is that the experiments are perfectly independent, as each flask is treated individually, and when they do support each other there is more assurance that the results are correct. The agreement of the results of a series is not what was desired, and sometimes the averages of two series do not agree as they might, but in nearly all cases the velocity is determined exactly enough to define clearly the relations of the various amides. The baryta water used was made up, 2 liters at a time, from a strong stock solution, and the strength of each lot determined by titration. 75 cc. of this were measured into each flask from an automatic pipette connected with the bottle and protected from the carbon dioxide of the air. In Series I the possibility of readily and completely decomposing, by means of strong alkali, the amides used, made it easier to employ the method previously used for *m*- and *p*-nitrobenzamides, that is, the amide was weighed into a large flask with 600 cc. baryta water and measured samples taken out. The free ammonia was distilled off with magnesium hydroxide and thrown away, and the residual amide estimated by distilling with strong caustic soda.

As for the remaining experiments, the effort was made to make them as nearly uniform as possible. The amide was, as before, weighed into the carefully cleaned and dried Erlenmeyer flasks. A large bottle full of rather strong baryta water was prepared and, by means of an automatic pipette, 17.56 cc. of this added to

each flask into which had just been put the water from two other automatic pipettes holding 6.87 and 50.57 cc., respectively, the three making just 75 cc. The water used had been distilled from acid chromate and alkaline permanganate solutions. The water and baryta solutions were well protected with soda-lime tubes both while in the pipettes and while in the containers. The baryta water, so diluted, was always perfectly clear in the flasks and showed no trace of carbonate. Many experiments were lost on account of the breaking of the flasks, the most fatal time being the moment when they were plunged into cold water to stop the reaction. Continued heating with baryta water etches the glass and renders it very brittle. The strength of the diluted baryta water was determined by titration. For this, and for the estimation of the ammonia, hydrochloric acid 14.66 N was used. To standardize this 0.500 gram *p*-nitrobenzamide was weighed into each of four distilling flasks, water and 5 grams of caustic soda added and distilled, the ammonia being caught in a measured portion of the acid to be standardized. One stopper was found to be defective and that flask rejected. The ammonia from the other three neutralized 20.55, 20.54, and 20.55 cc., respectively, of the acid. 20.55 cc. of the acid was taken to be equivalent to 0.500 gram *o*-nitrobenzamide and as, with few exceptions, the amount of amide used in any experiment was equivalent to that, this figure was used directly in calculating the per cent of decomposition. I would like to recommend this method of standardizing acid, to chemists in general, and especially to those engaged on ammonia work, who have the stills already set up. To one so prepared, it is the quickest and simplest that I know of, and gives results under the actual working conditions with the same amounts of materials, indicators and the like as are employed in the usual determinations. Paranitrobenzamide is particularly well adapted for such service. It need not be weighed with extreme care since owing to its rather high molecular weight, it yields, on hydrolysis, only a little over 10 per cent of its weight of ammonia. Paranitrobenzoic acid is a commercial article or may be easily and cheaply prepared by the pound, from commercial paranitrotoluene. It is purified by one crystallization or



even by solution in soda and precipitation of the filtered solution by acid. It is readily converted into the amide. The amide crystallizes well from hot water, in which it is only slightly soluble, and may be obtained perfectly pure at one crystallization. It forms, when the water solution is rapidly cooled, dense fine grains easy to weigh and contains no water of crystallization. It is easily identified by its melting-point, and as it melts at  $201^{\circ}.4$  C., it may safely be dried in an air-bath. It yields the calculated amount of ammonia when distilled in the usual way with alkali, just as readily and as surely as an equivalent amount of any ammonium salt. It may be kept for years without alteration.

## SERIES I.

$\text{Ba}(\text{OH})_2 = A = 0.0984$ ,  $B = 0.04026$ ,  $A - B = 0.0581$ ,

$A/B = 2.445$ . Temp.  $100^{\circ}$  C.

*m*-Amidobenzamide, 3.712 Grams.

<i>t</i>	Un- changed.	Volume of sample.	Equiva- lent of sample.	Per cent changed, <i>x</i> .	$A - x$ .	$B - x$ .	<i>K</i> .	<i>K</i> (cor.).
30	15.64	70.5	19.81	21.1	223.4	78.9	0.0836	0.0869
60	12.12	70.5	19.81	38.8	205.7	61.2	0.0907	0.0943
90	10.57	73.7	20.71	49.0	195.5	51.0	0.0854	0.0888
120	8.61	73.6	20.68	58.4	186.1	41.6	0.0860	0.0894
150	7.04	73.2	20.56	65.8	178.7	34.2	0.0866	0.0900
180	6.04	74.9	21.02	71.3	173.2	28.7	0.0858	0.0892
210	5.26	74.6	20.96	74.9	169.6	25.1	0.0827	0.0860
240	4.97	80.1	22.50	77.9	166.6	22.1	0.0802	0.0834

*m*-Toluicamide, 3.256 Grams.

30	15.58	71.9	20.20	22.9	221.6	77.1	0.0921	0.0958
60	12.35	72.1	20.25	39.0	205.5	61.0	0.0913	0.0945
90	10.50	69.3	19.47	46.1	198.4	53.9	0.0777	0.0808
120	8.57	67.5	18.96	54.8	189.7	45.2	0.0770	0.0801
150	7.60	71.5	20.08	62.2	182.3	37.8	0.0774	0.0805
180	6.47	69.1	19.41	66.7	177.8	33.3	0.0742	0.0772
210	6.08	74.1	20.82	70.3	174.2	29.7	0.0712	0.0740
240	6.08	86.3	24.21	74.9	169.6	25.1	0.0724	0.0753

*p*-Toluicamide, 3.256 Grams.

30	15.12	63.8	17.92	15.6	228.9	84.4	0.0591	0.0615
60	13.01	69.3	19.47	33.2	211.3	66.8	0.0734	0.0763
90	11.94	71.5	20.08	40.5	204.0	59.5	0.0642	0.0668
120	11.86	71.4	20.06	41.9	202.6	58.1	0.0506	0.0526
150	9.09	74.7	21.00	56.7	187.8	43.3	0.0653	0.0679
180	8.63	77.5	21.77	60.4	184.1	39.6	0.0610	0.0634
210	7.20	73.5	20.65	65.1	179.4	34.9	0.0605	0.0629
240	6.20	66.3	18.63	66.8	177.7	33.2	0.0588	0.0612

In Series II, and in those that follow, the volume of the sample is always 75 cc. as the whole contents of the small flask is used and the equivalent of the sample 20.55 for the usual concentration or 10.27 for half concentration. For this reason the two columns containing these values are omitted. The second column gives the number of cubic centimeters of standard acid that the ammonia from the hydrolyzed amide neutralized. The other columns are the same as in the series above. In the first six series the temperature, when known exactly, is put at the beginning of the series. In those that follow, the temperature is put in the second column of figures, and to save figures it is given as the amount, in degrees, above  $100^{\circ}\text{C.}$ , using the minus sign when below. This temperature correction was found from the barometer reading.

#### SERIES II.

$\text{Ba}(\text{OH})_2 = A = 0.1012$ ,  $B = 0.04026$ ,  $A - B = 0.0609$ ,  $A/B = 2.514$ . Temp.  $89^{\circ}.89\text{ C.}$

*o-Toluicamide, 0.407 Gram.*

<i>t.</i>	Changed.	Per cent changed, <i>x</i> .	<i>A</i> - <i>x</i> .	<i>B</i> - <i>x</i> .	<i>K</i> .	<i>K</i> (cor.).
30	0.42	2.0	249.4	98.0	0.00669	0.00699
60	0.66	3.1	248.3	96.9	0.00522	0.00546
90	0.85	4.0	247.4	96.0	0.00454	0.00475
120	1.00	4.8	246.6	95.2	0.00408	0.00426
150	1.79	7.1	244.3	92.9	0.00492	0.00514
180	1.88	8.9	242.5	91.1	0.00522	0.00546
210	1.98	9.4	242.0	90.6	0.00473	0.00494
240	2.29	10.8	240.6	89.2	0.00480	0.00502

*o-Chlorbenzamide, 4.688 Grams. Temp.  $100^{\circ}.02\text{ C.}$*

30	2.61	12.4	239.0	87.6	0.0447	0.0464
60	4.67	22.1	229.3	77.9	0.0431	0.0448
120	7.62	36.1	215.3	63.9	0.0401	0.0417
150	9.13	43.3	208.1	56.7	0.0439	0.0456
180	10.75	50.9	200.5	49.1	0.0380	0.0395
240	12.25	58.0	133.4	42.0	0.0414	0.0430

## SERIES III.

$\text{Ba}(\text{OH})_2 = A = 0.1030$ ,  $B = 0.04026$ ,  $A - B = 0.0627$ ,  $A/B = 2.559$ .

*o*-Hydroxybenzamide, 0.416 Gram. Temp.  $100^\circ.02$  C.

<i>t</i> .	Changed.	Per cent changed, <i>x</i> .	<i>A</i> — <i>x</i> .	<i>B</i> — <i>x</i> .	<i>K</i> .	<i>K</i> (cor.).
30	0.66	3.1	252.8	96.9	0.01149	0.01193
60	0.93	4.4	251.5	95.6	0.00723	0.00751
90	1.26	6.0	249.9	94.0	0.00646	0.00671
120	1.42	6.8	249.1	93.2	0.00576	0.00598
150	1.68	8.0	247.9	92.0	0.00547	0.00568
180	2.04	9.7	246.2	90.3	0.00562	0.00584
240	2.42	11.5	244.4	88.5	0.00507	0.00527

*Benzamide*, 0.365 Gram. Temp.  $99^\circ.92$  C.

30	4.93	23.4	233.2	76.6	0.0905	0.0945
60	8.48	40.2	216.4	59.8	0.0909	0.0949
90	10.07	52.5	204.1	47.5	0.0909	0.0949
120	12.96	61.4	195.2	38.6	0.0897	0.0936
150	14.28	67.7	188.9	32.3	0.0872	0.0910
180	15.06	71.4	185.2	28.6	0.0816	0.0852

## SERIES IV.

$\text{Ba}(\text{OH})_2 = A = 0.1097$ ,  $B = 0.04026$ ,  $A - B = 0.0694$ ,  $A/B = 2.725$ .

*o*-Nitrobenzamide, 0.500 Gram. Temp.  $99^\circ.84$  C.

30	3.03	14.2	259.3	85.8	0.0491	0.0522
60	4.82	22.6	249.9	77.4	0.0407	0.0427
90	6.41	30.1	242.4	69.9	0.0386	0.0405
120	7.33	34.4	238.1	65.6	0.0345	0.0362
150	7.90	37.1	235.4	62.9	0.0305	0.0320
180	8.58	40.3	232.2	59.7	0.0285	0.0299
210	9.15	43.0	229.5	57.0	0.0268	0.0281
240	9.80	46.0	226.5	54.0	0.0256	0.0272

*m*-Nitrobenzamide, 0.500 Gram. Temp.  $100^\circ$  C.

30	17.23	81.0	191.0	19.0	0.627	0.652
60	19.65	92.4	180.1	7.6	0.519	0.540
90	20.63	97.0	175.5	3.0	0.491	0.511

## SERIES V.

$\text{Ba}(\text{OH})_2 = A = 0.1033, B = 0.04026, A - B = 0.0630, A/B = 2.566.$

*p*-Amidobenzamide, 0.410 Gram. Temp. 100° C.

<i>t</i> .	Changed.	Per cent changed, <i>x</i> .	<i>A</i> — <i>x</i> .	<i>B</i> — <i>x</i> .	<i>K</i> .	<i>K</i> (cor.).
30	1.40	6.6	250.0	93.4	0.0223	0.0232
60	2.38	11.2	245.4	88.8	0.0196	0.0204
90	3.53	16.6	240.0	83.4	0.0202	0.0210
120	4.47	21.0	235.6	79.0	0.0199	0.0207
180	6.19	29.1	227.5	70.9	0.0197	0.0205
210	6.76	31.7	224.9	68.3	0.0189	0.0197
240	7.36	34.5	222.1	65.5	0.0184	0.0192

## SERIES VI.

$\text{Ba}(\text{OH})_2 = A = 0.1030, B = 0.04026, A - B = 0.0627, A/B = 2.559.$

*o*-Iodobenzamide, 0.743 Gram. Temp. 99°.75 C.

30	1.06	5.0	250.9	95.0	0.0168	0.0177
60	1.79	8.4	247.5	91.6	0.0144	0.0151
90	2.31	10.8	245.1	89.2	0.0126	0.0133
150	3.59	16.8	239.1	83.2	0.0123	0.0129
180	4.05	19.0	236.9	81.0	0.0118	0.0124
210	4.49	21.1	234.8	78.9	0.0115	0.0121
240	5.08	23.9	232.0	76.1	0.0116	0.0122

*o*-Methoxybenzamide, 0.455 Gram. Temp. 100° C.

60	5.51	25.9	230.0	74.1	0.0514	0.0534
120	9.11	42.9	213.0	57.1	0.0501	0.0521
150	10.19	47.0	208.9	53.0	0.0460	0.0478
180	11.72	55.1	200.8	44.9	0.0495	0.0515
210	13.16	61.9	194.0	38.1	0.0523	0.0544
240	13.88	65.3	190.6	34.7	0.0508	0.0528

*p*-Methoxybenzamide, 0.455 Gram. Temp. 99°.67 C.

60	5.09	23.6	232.3	76.4	0.0455	0.0480
90	7.03	33.0	222.9	67.0	0.0465	0.0491
120	8.55	40.1	215.8	59.9	0.0442	0.0467
180	10.50	49.4	206.5	50.6	0.0417	0.0440
210	11.68	54.9	201.0	45.1	0.0421	0.0445
240	12.76	60.1	195.8	39.9	0.0426	0.0450

## SERIES VI (Continued).

*o*-Ethoxybenzamide, 0.497 Gram. Temp. 100° C.

<i>t.</i>	Changed.	Per cent changed, <i>x</i> .	<i>A</i> - <i>x</i> .	<i>B</i> -- <i>x</i> .	<i>K</i> .	<i>K</i> (cor.)
120	7.00	32.9	223.0	67.1	0.0347	0.0361
180	9.42	44.2	211.7	55.8	0.0349	0.0363
240	11.14	52.4	203.5	47.6	0.0341	0.0355

*o*-Dimethylamidobenzamide, 0.494 Gram. Temp. 100° C.

60	1.88	8.8	247.1	91.2	0.0152	0.0158
120	3.49	16.4	239.5	83.6	0.0150	0.0156
150	4.12	19.3	236.6	80.7	0.0145	0.0151
180	4.65	21.8	234.1	78.2	0.0139	0.0145
210	5.48	25.7	230.2	74.3	0.0145	0.0151
240	6.02	28.3	227.6	71.7	0.0144	0.0150

*m*-Hydroxybenzamide, 0.416 Gram. Temp. 100° C.

60	1.56	7.4	248.5	92.6	0.0126	0.0131
90	2.53	12.0	243.9	88.0	0.0141	0.0147
150	5.02	23.8	232.1	76.2	0.0185	0.0192
180	6.00	28.4	227.5	71.6	0.0191	0.0199
210	6.47	30.6	225.3	69.4	0.0181	0.0189
240	7.08	33.5	222.9	66.5	0.0159	0.0165

## SERIES VII.

*Benzamide, 0.365 Gram.*

$\text{Ba}(\text{OH})_2 = A = 0.10416$ ,  $B = 0.04026$ ,  $A - B = 0.0639$ ,  $A/B = 2.592$ .

<i>t</i> .	Temperature correction.	Changed.	Per cent changed, <i>x</i> .	<i>A</i> — <i>x</i> .	<i>B</i> — <i>x</i> .	<i>K</i> .	<i>K</i> (cor.).
30	—0.01	4.14	20.1	239.1	79.9	0.0751	0.0781
60	"	8.55	41.6	217.6	58.4	0.0944	0.0982
90	"	11.07	53.9	205.3	46.1	0.0941	0.0979
120	"	13.18	64.1	195.1	35.9	0.0965	0.1004
150	"	14.73	71.7	187.5	28.3	0.0979	0.1018
210	"	16.57	80.6	178.6	19.4	0.0944	0.0982
270	—0.34	17.61	85.7	173.5	14.3	0.0895	0.0945
300	"	18.00	87.6	171.6	12.4	0.0874	0.0954
330	"	18.35	89.5	169.7	10.5	0.0868	0.0917
360	"	19.14	93.1	166.1	6.9	0.0969	0.1023
30	"	4.48	21.8	237.4	78.2	0.0824	0.0871
60	"	7.89	38.4	220.8	61.6	0.0845	0.0893
90	"	10.69	52.0	207.2	48.0	0.0887	0.0937
120	"	12.72	61.9	197.3	38.1	0.0903	0.0954
150	"	14.10	68.6	190.6	31.4	0.0888	0.0938
180	"	15.27	74.3	184.9	25.7	0.0887	0.0938
210	"	16.26	79.1	180.1	20.9	0.0895	0.0946
240	"	16.95	82.5	176.7	17.5	0.0887	0.0937

*p*-Amidobenzamide, 0.410 Gram.

30	..	1.20	5.8	253.4	94.2	0.0194	0.0202
60	..	2.05	10.0	249.2	90.0	0.0172	0.0179
90	..	3.05	14.8	244.3	85.1	0.0170	0.0176
120	..	3.80	18.5	240.7	81.5	0.0170	0.0177
150	..	4.58	22.3	236.9	77.7	0.0169	0.0176
180	..	5.42	26.4	232.8	73.6	0.0173	0.0180
210	..	6.05	29.4	229.8	70.6	0.0168	0.0174
240	..	6.11	29.7	229.5	70.3	0.0150	0.0156
300	—0.08	8.41	40.9	218.3	59.1	0.0185	0.0193
360	0.00	9.27	45.1	214.1	54.9	0.0178	0.0185
420	—0.08	10.21	49.7	209.5	50.3	0.0177	0.0185
450	0.00	10.43	50.7	208.5	49.3	0.0170	0.0177
480	0.00	10.65	51.8	207.4	48.2	0.0165	0.0172
540	..	11.87	57.8	204.1	42.2	0.0177	0.0184
840	..	14.38	70.0	189.2	30.0	0.0166	0.0172

## SERIES VII (Continued).

*m*-Amidobenzamide, 0.464 Gram.

<i>t</i> .	Temperature correction.	Changed.	Per cent changed, <i>x</i> .	<i>A</i> - <i>x</i> .	<i>B</i> - <i>x</i> .	<i>K</i> .	<i>K</i> (cor.).
31½	0.11	4.79	23.3	235.9	76.7	0.0893	0.0922
60	"	7.92	36.4	222.8	63.6	0.0786	0.0811
90	"	10.33	50.3	208.9	49.7	0.0840	0.0867
150	"	13.82	67.3	191.9	32.7	0.0853	0.0880
180	"	15.14	73.7	185.5	26.3	0.0870	0.0899
210	"	16.05	78.1	181.1	21.9	0.0864	0.0893
240	"	16.70	81.3	177.9	18.7	0.0848	0.0876

*o*-Chlorbenzamide, 0.468 Gram.

30	0.07	2.82	13.7	245.5	86.3	0.0485	0.0503
60	"	5.21	25.4	233.8	74.6	0.0495	0.0501
150	"	9.94	48.4	210.8	51.6	0.0475	0.0492
180	"	10.91	53.1	206.1	46.9	0.0459	0.0475
210	"	11.67	56.8	202.4	43.2	0.0441	0.0457
240	"	12.89	62.7	196.5	37.3	0.0462	0.0479
270	"	14.04	68.3	190.9	31.7	0.0489	0.0506
300	"	14.47	70.4	188.8	29.6	0.0470	0.0486
330	"	15.25	74.2	185.0	25.8	0.0482	0.0500
360	"	15.65	76.2	183.0	23.8	0.0473	0.0490

*o*-Hydroxybenzamide, 0.416 Gram.

30	-0.12	0.54	2.6	256.6	97.4	0.0085	0.0088
60	"	0.84	4.1	255.1	95.9	0.0068	0.0070
90	"	1.20	5.8	253.4	94.2	0.0064	0.0067
120	"	1.46	7.1	252.1	92.9	0.0060	0.0062
150	"	1.62	7.9	251.3	92.1	0.0054	0.0056
180	"	1.84	9.0	250.2	91.0	0.0051	0.0053
210	"	2.23	10.9	248.3	89.1	0.0054	0.0056
240	"	2.50	12.2	247.0	87.8	0.0053	0.0055
330	"	3.06	14.9	244.3	85.1	0.0048	0.0050
360	"	3.35	16.3	242.9	83.7	0.0049	0.0051
390	"	3.44	16.7	242.5	83.3	0.0046	0.0048
420	"	3.55	17.3	241.9	82.7	0.0045	0.0047

*o*-Brombenzamide, 0.602 Gram.

60	-0.09	3.31	16.1	243.1	83.9	0.0290	0.0302
120	"	5.85	28.5	230.7	71.5	0.0286	0.0297
180	"	7.62	37.1	222.1	62.9	0.0269	0.0280
240	"	9.30	45.3	213.9	54.3	0.0273	0.0284

SERIES VII (Continued).  
*m*-Toluicamide, 0.407 Gram.

<i>t</i> .	Temperature correction.	Changed.	Per cent changed, <i>x</i> .	<i>A</i> — <i>x</i> .	<i>B</i> — <i>x</i> .	<i>K</i> .	<i>K</i> (Cor.).
30	—0.19	3.73	18.2	241.0	81.8	0.0668	0.0701
60	"	7.03	34.2	225.0	65.8	0.0722	0.0756
90	—0.34	9.19	44.7	214.5	55.3	0.0701	0.0712
120	"	10.64	51.8	207.4	48.2	0.0661	0.0697
150	—0.19	13.42	65.3	193.9	34.7	0.0801	0.0846
180	"	14.36	69.9	189.3	30.1	0.0771	0.0814
210	"	15.04	73.2	186.0	26.8	0.0734	0.0745
240	"	15.84	77.1	182.1	22.9	0.0731	0.0742

*m*-Brombenzamide, 0.602 Gram.

30	0.08	10.52	51.2	208.0	48.8	0.259	0.272
60	"	15.13	73.6	185.6	26.4	0.260	0.273
90	"	17.54	85.4	173.8	14.6	0.265	0.278
120	"	18.73	91.1	168.1	8.9	0.259	0.271

SERIES VIII.

$$\text{Ba(OH)}_2 = A = 0.10416, B = 0.03746, A - B = 0.0667, A/B = 2.800.$$

*p*-Toluicamide, 0.379 Gram.

30½	0.16	3.12	16.3	263.7	83.7	0.0589	0.0607
60	"	5.47	28.6	251.4	71.4	0.0572	0.0591
90	"	7.36	38.5	241.5	61.5	0.0563	0.0582
120	"	9.07	47.4	232.6	52.6	0.0571	0.0590
180	"	11.73	61.4	218.6	38.6	0.0586	0.0606
210	"	12.61	65.9	214.1	34.1	0.0576	0.0596
240	"	13.44	70.3	209.7	29.7	0.0578	0.0597

*o*-Toluicamide, 0.379 Gram.

30	0.13	0.31	1.6	278.4	98.4	0.0052	0.0053
60	"	0.59	3.1	276.9	96.9	0.0051	0.0053
90	"	0.90	4.7	275.3	95.3	0.0052	0.0054
120	"	1.06	5.5	274.5	94.5	0.0046	0.0048
150	"	1.39	7.3	272.7	92.7	0.0049	0.0051
180	"	1.54	8.6	271.4	91.4	0.0049	0.0051
210	"	1.91	10.0	270.0	90.0	0.0049	0.0051
240	"	1.99	10.4	269.6	89.6	0.0046	0.0047
630	"	2.68	14.0	266.0	86.0	0.0045	0.0047
660	"	2.94	15.4	264.6	84.6	0.0046	0.0048



## SERIES IX.

$$\text{Ba(OH)}_2 = A = 0.10416, \quad B = 0.02013, \quad A - B = 0.08403, \\ A/B = 5.184.$$

*m*-Brombenzamide, 0.301 Gram.

<i>t</i> .	Temperature correction.	Changed.	Per cent changed, <i>x</i> .	<i>A</i> - <i>x</i> .	<i>B</i> - <i>x</i> .	<i>K</i> .	<i>K</i> (Cor.).
30	-0.07	5.61	54.6	463.8	45.4	0.275	0.287
60	"	7.92	77.1	441.3	22.9	0.267	0.278
90	"	9.04	88.0	430.4	12.0	0.262	0.273
120	"	9.57	93.1	425.3	6.9	0.251	0.262
150	"	10.03	97.6	420.8	2.4	0.286	0.298
180	"	10.14	98.7	419.7	1.3	0.280	0.292

*m*-Iodobenzamide, 0.371 Gram.

30	0.13	5.90	57.4	461.0	42.6	0.299	0.310
60	"	7.58	73.5	444.9	26.5	0.239	0.248
90	"	8.72	84.9	433.5	15.1	0.232	0.240
120	"	9.52	92.7	425.7	7.3	0.246	0.254
150	"	9.77	95.1	423.3	4.9	0.228	0.237

*p*-Chlorbenzamide, 0.234 Gram.

30	-0.13	4.86	47.3	471.1	52.7	0.221	0.231
60	"	6.92	67.3	451.1	32.7	0.199	0.208
90	"	7.61	74.1	444.3	25.7	0.162	0.169
120	"	8.72	84.9	433.5	15.1	0.174	0.182
150	"	9.22	89.7	428.7	10.3	0.169	0.177
180	"	9.73	94.7	423.7	5.3	0.185	0.193
210	"	9.82	95.6	422.8	4.4	0.169	0.177
240	"	9.97	97.0	421.4	3.0	0.167	0.175
30	0.00	4.11	40.0	478.4	60.0	0.175	0.182
60	"	6.40	63.3	455.1	36.7	0.177	0.184
90	"	7.64	74.4	444.0	25.6	0.163	0.170
120	"	8.69	84.6	433.8	15.4	0.172	0.179
180	"	9.57	93.1	425.3	6.9	0.168	0.175
210	"	9.75	94.9	423.5	5.1	0.161	0.167

## SERIES IX (Continued).

*p*-Brombenzamide, 0.301 Gram.

<i>t</i> .	Temperature correction.	Changed.	Per cent changed, <i>x</i> .	<i>A</i> - <i>x</i> .	<i>B</i> - <i>x</i> .	<i>K</i> .	<i>K</i> (Cor.).
30	—0.08	4.14	40.3	478.1	59.7	0.177	0.185
60	“	6.64	64.6	453.8	35.4	0.184	0.192
90	“	8.22	80.0	438.4	20.0	0.195	0.204
120	“	8.86	86.2	432.2	13.8	0.183	0.191
150	“	9.33	90.8	427.6	9.2	0.178	0.186
180	“	9.58	93.2	425.2	6.8	0.168	0.176
30	0.00	4.04	39.3	479.1	60.7	0.171	0.177
60	“	6.36	61.9	456.5	38.1	0.170	0.177
90	“	7.79	75.8	442.6	24.2	0.171	0.177
180	“	9.45	92.0	426.4	8.0	0.158	0.164
210	“	9.61	93.5	424.9	6.5	0.147	0.153

*p*-Iodobenzamide, 0.371 Gram.

30	—0.13	3.59	34.9	483.5	65.1	0.146	0.153
60	“	5.89	57.3	461.1	42.7	0.149	0.156
90	“	7.52	73.2	445.2	26.8	0.158	0.165
120	“	8.44	82.1	436.3	17.9	0.157	0.164

*o*-Phenoxybenzamide, 0.321 Gram.

30	—0.01	1.25	12.2	506.2	87.8	0.0422	0.0439
60	“	2.32	22.6	495.8	77.4	0.0420	0.0437
90	“	3.16	30.8	487.6	69.2	0.0406	0.0422
180	“	5.05	49.1	469.3	50.9	0.0350	0.0364
210	“	5.81	56.5	461.9	43.5	0.0406	0.0423
240	“	6.11	59.5	458.9	40.5	0.0386	0.0402
270	“	6.72	65.4	453.0	34.6	0.0408	0.0425
360	“	7.81	76.0	442.4	24.0	0.0419	0.0436
420	“	8.40	81.7	436.7	18.3	0.0433	0.0450
450	“	8.31	80.9	437.5	19.1	0.0394	0.0410

## SERIES X.

*o*-Nitrobenzamide, 0.500 Gram.

$\text{Ba}(\text{OH})_2 = A = 0.10416$ ,  $B = 0.04026$ ,  $A - \frac{1}{2}B = 0.08403$ ,  
 $A/\frac{1}{2}B = 5.184$ . Temp.  $100^\circ \text{C}$ .

<i>t</i> .	Changed.	Per cent changed, <i>x</i> .	$A - 2x$ .	$B - 2x$ .	<i>K</i> (Cor.).
30	2.67	13.0	492.4	74.0	0.1054
60	4.52	22.0	474.4	56.0	0.1036
90	5.90	28.7	461.0	42.6	0.1021
120	6.65	32.4	453.6	35.2	0.0961
150	7.53	36.6	445.2	26.8	0.0983
180	8.02	39.0	440.4	22.0	0.0951
210	8.49	41.3	435.8	17.4	0.0947
240	8.87	43.2	432.0	13.6	0.0956
300	9.34	45.6	427.2	8.8	0.0944
360	9.99	48.6	421.2	2.8	(0.1185)
420	9.93	48.3	421.8	3.4	0.0957
480	10.31	50.1	....	....	....
900	10.21	49.7	....	....	....
1500	10.03	48.8	....	....	....

## RECAPITULATION.

Constants of Amides with Barium Hydrate.—Constant of Benzamide, 0.0943.

<i>o</i> -Toluic.	<i>o</i> -Nitro-	<i>o</i> -Chlor-	<i>o</i> -Hydroxy-	<i>o</i> -Brom-	<i>o</i> -Iodo-
(0.00699)	0.0522	0.0464	(0.01193)	0.0302	0.0177
0.00546	0.0427	0.0448	0.00751	0.0297	0.0151
0.00475	0.0405	0.0417	0.00671	0.0280	0.0133
0.00426	0.0362	0.0456	0.00598	0.0284	0.0129
0.00514	0.0320	0.0395	0.00568	....	0.0124
0.00546	0.0299	0.0430	0.00584	....	0.0121
0.00494	0.0281	....	0.00527	....	0.0122
0.00502	0.0272	....	....	....	....
<hr/>		<hr/>		<hr/>	
0.00508		0.0435	0.00616	0.0291	0.0130

RECAPITULATION (*Continued*).

<i>o</i> -Hydroxy-	<i>o</i> -Methoxy-	<i>o</i> -Ethoxy-	<i>o</i> -Dimethylamido-	<i>o</i> -Phenoxy- $\frac{1}{2}$ Conc.	<i>o</i> -Toluic.
0.0088	0.0534	0.0361	0.0158	0.0439	0.0053
0.0070	0.0521	0.0363	0.0156	0.0437	0.0053
0.0067	0.0478	0.0355	0.0151	0.0422	0.0054
0.0062	0.0515	....	0.0145	0.0364	0.0048
0.0056	0.0544	....	0.0151	0.0423	0.0051
0.0053	0.0528	....	0.0150	0.0402	0.0051
0.0056	....	....	....	0.0425	0.0051
0.0055	....	....	....	0.0436	0.0047
0.0050	....	....	....	0.0450	0.0047
0.0051	....	....	....	0.0410	0.0048
0.0048	....	....	....	....	....
0.0047	....	....	....	....	....
<hr/>					
0.0059?	0.0528	0.0360	0.0152	0.0427	0.00503

RECAPITULATION (*Continued*).

<i>o</i> -Chlor-	Benzamide.	Benzamide.	<i>m</i> -Amido-	<i>m</i> -Amido-	<i>p</i> -Amido-
0.0503	0.0945	0.0945	0.0922	0.0869	(0.0202)
0.0501	0.0949	0.0954	0.0811	0.0943	0.0179
0.0492	0.0949	0.0917	0.0861	0.0888	0.0176
0.0475	0.0936	0.1023	0.0880	0.0894	0.0177
0.0457	0.0910	0.0871	0.0899	0.0900	0.0176
0.0479	0.0852	0.0893	0.0893	0.0892	0.0180
0.0506	0.0781	0.0937	0.0876	0.0860	0.0174
0.0486	0.0982	0.0954	....	0.0834	0.0156
0.0500	0.0979	0.0938	....	....	0.0193
0.0490	0.1004	0.0938	....	....	0.0185
....	0.1018	0.0946	....	....	0.0185
....	0.0982	0.0937	....	....	0.0177
....	....	....	....	....	0.0172
....	....	....	....	....	0.0184
....	....	....	....	....	0.0172
<hr/>					
0.0489	0.0943		0.0877	0.0885	0.0178

RECAPITULATION (*Continued*).

<i>p</i> -Chlor- $\frac{1}{2}$ Conc.	<i>p</i> -Brom- $\frac{1}{2}$ Conc.	<i>m</i> -Brom- $\frac{1}{2}$ Conc.	<i>m</i> -Brom- Regular conc.	<i>p</i> -Iodo- $\frac{1}{2}$ Conc.	<i>m</i> -Iodo- $\frac{1}{2}$ Conc.	<i>m</i> -Nitro-
(0.231)	0.185	0.287	0.272	0.153	0.310	0.652
0.208	0.192	0.278	0.273	0.156	0.248	0.540
0.169	0.204	0.273	0.278	0.165	0.240	0.511
0.182	0.191	0.262	0.271	0.164	0.254	....
0.177	0.186	0.298	....	....	0.237	....
0.193	0.176	0.292	....	....	....	....
0.177	0.177	....	....	....	....	....
0.175	0.177	....	....	....	....	....
0.182	0.177	....	....	....	....	....
0.184	0.164	....	....	....	....	....
0.170	0.153	....	....	....	....	....
0.179	....	....	....	....	....	....
0.175	....	....	....	....	....	....
0.167	....	....	....	....	....	....
....	....	....	....	....	....	....
0.180	0.180	0.282	0.273	0.159	0.245	0.530

RECAPITULATION (*Continued*).

<i>m</i> -Toluic-	<i>m</i> -Toluic-	<i>p</i> -Toluic-	<i>p</i> -Toluic-	<i>p</i> -Amido-	<i>p</i> -Methoxy-	<i>m</i> -Hydroxy-
0.0958	0.0701	0.0615	0.0607	0.0232	0.0480	0.0131
0.0945	0.0756	0.0763	0.0591	0.0204	0.0491	0.0147
0.0808	0.0712	0.0668	0.0582	0.0210	0.0467	0.0192
0.0801	0.0697	0.0526	0.0590	0.0207	0.0440	0.0199
0.0805	0.0846	0.0679	0.0606	0.0205	0.0445	0.0189
0.0772	0.0814	0.0634	0.0596	0.0197	0.0450	0.0165
0.0740	0.0745	0.0629	0.0597	0.0192	....	....
0.0753	0.0742	0.0612	....	....	....	....
0.0780	0.0752	0.0623	0.0596	0.0202	0.0462	0.0180

*Summary of Average Velocities with Barium Hydrate.*

For the sake of whole numbers all of the above averages are multiplied by 10,000.

*Benzamide, 944.*

<i>o</i> -Cl 489	<i>o</i> -Br 291	<i>o</i> -I 130	....
<i>o</i> -OH 60	<i>o</i> -OCH <sub>3</sub> 528	<i>o</i> -OC <sub>2</sub> H <sub>5</sub> 360	<i>o</i> -OC <sub>6</sub> H <sub>5</sub> 427
<i>o</i> -CH <sub>3</sub> 50.5	<i>o</i> -N(CH <sub>3</sub> ) <sub>2</sub> 152	....	....
....	<i>m</i> -Br 2820	<i>m</i> -I 2450	<i>m</i> -NO <sub>2</sub> 5300
<i>p</i> -Cl 1800	<i>p</i> -Br 1800	<i>p</i> -I 1590	( <i>p</i> -NO <sub>2</sub> 6300)
<i>m</i> -NH <sub>2</sub> 885	<i>m</i> -CH <sub>3</sub> 752	<i>m</i> -OH 165	....
<i>p</i> -NH <sub>2</sub> 178	<i>p</i> -CH <sub>3</sub> 623	....	<i>p</i> -OCH <sub>3</sub> 462

*Discussion of Results.*

As seen from the above tables, the decomposition velocities of the various amides show a much wider range of variation with alkali than with acid. As already remarked, there is more difficulty in getting uniform results in a series and, in several cases, a series recently made does not agree very well with one previously made. Seemingly erratic individual results have been thrown out in making up averages, and of two series, the most recent has been chosen. In nearly every series there is noticed a more or less regular falling off in the velocity as the reaction proceeds. This is to be expected from the known retarding action of salts which accumulate in the course of the reaction. The first measurement in a series often comes out much too high. In the experiments with *o*-hydroxybenzamide the velocity seems to decrease much too rapidly. This is borne out by two independent series. It may be that the reaction is of a different type and does not obey the equation assumed. Perhaps the acid hydroxyl group has something to do with this irregularity. With the concentrations used, the velocity of the reaction is rather small for convenient study but the case might repay a more thorough investigation. With alkali, as with acid, ortho substituted amides give low velocities. Among the halogens, chlorine retards much less than bromine which, in turn, retards far less than iodine. The methyl and hydroxyl groups are remarkable for their great effect. The ethoxy group retards more than the methoxy and even more than the phenoxy, though none of the three is in the same category with hydroxyl. The methoxy group, in the ortho position, retards only 44.0 per cent while hydroxyl, in the same place, retards 93.6 per cent. As concerns meta and para substituted amides, the results fall into three classes. First those in which there is a moderate retardation, the group having more influence in the para than in the meta position. This includes the toluic amides and metamidobenzamide. Second, those in which the groups exercise a large retarding influence. The most conspicuous of these is hydroxybenzamide while the amido group in the para position cuts the velocity down to less than one-

fourth of its normal value. The methoxy group stands alone in that it retards more when in the para than when in the ortho position, the velocities being 462 and 528, respectively. In the work with acid, the methoxy group in the para position was remarkable for its great influence, retarding almost as much as when in the ortho position, the velocities being 131 and 121, respectively. The third class of amides contains those having the nitro group or one of the halogens in the meta or para position. Those with the halogens are hydrolyzed two or three times as fast as benzamide, the meta being well ahead, while the nitro group quickens the reaction five and a half times when in the meta position and six and a half times in the para. The velocity here given for *p*-nitrobenzamide is calculated from that of the meta and the known relation of the meta and para at 90° C., as found in previous work. Paranitrobenzamide is less stable than the meta under the influence of both acids and alkalies. This and previous work goes to show that, with one exception to be noted presently, the hydrolysis of all the substituted benzamides proceeds regularly and in accordance with the equation assumed both in the presence of acids and alkalies. At the same concentration, baryta water acts usually some five or ten times as fast as hydrochloric acid. This is in contrast to statements based on merely qualitative experiments, such as that of Kolbe,<sup>1</sup> that orthoamidobenzamide is slowly saponified by caustic soda, easily by hydrochloric acid. As stated in the first article, I have boiled each of the amides studied with water and precipitated magnesium hydroxide for hours at a time and could never detect, either with litmus or with cochineal, even the slightest traces of ammonia in the distillate. In view of this, Engler's statement, "metabrombenzamide easily goes into acid with hot water," must be modified.<sup>2</sup> The results obtained with orthonitrobenzamide are not mentioned in the above as they seem so anomalous as to require special mention. In the one series given in the summary, it will be seen that the velocity decreases from 0.0522 to 0.0272. The shape of the curve given by plotting these results is also

<sup>1</sup> J. prakt. Chem. (2), 30, 476.

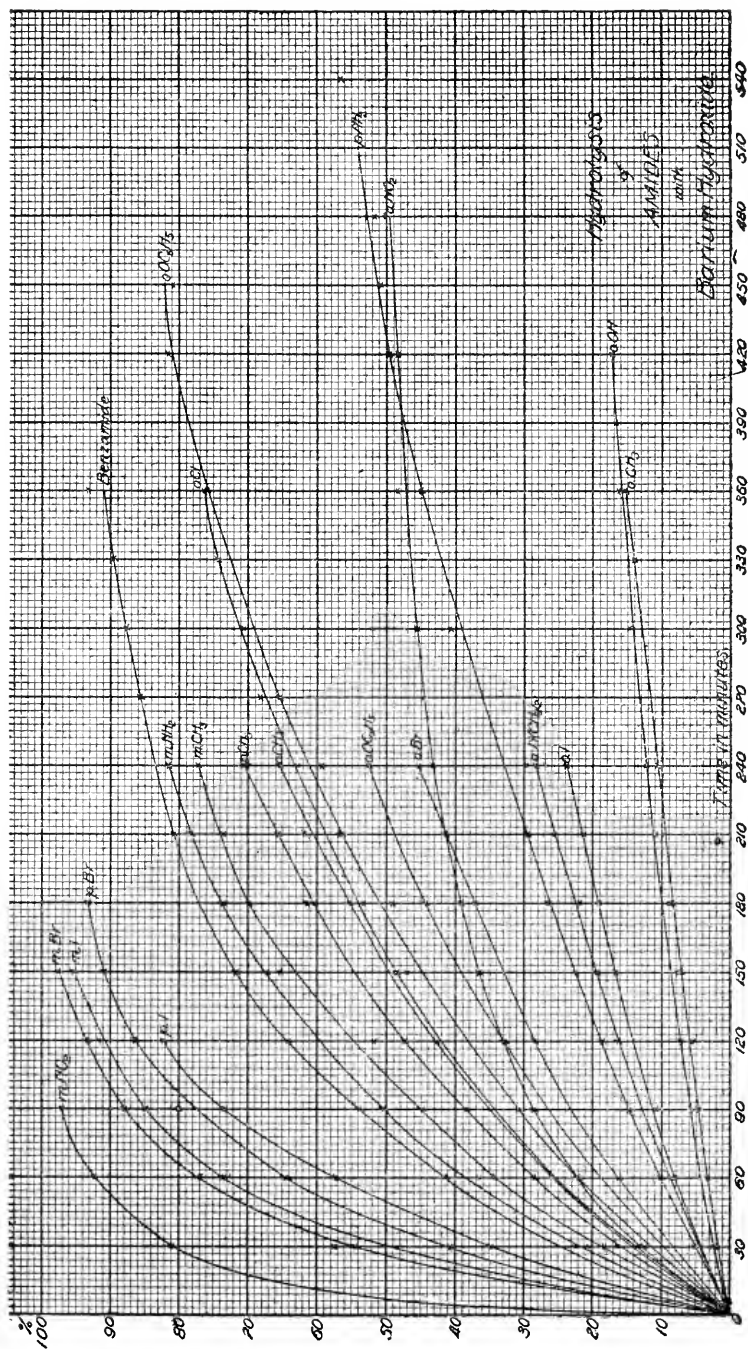
<sup>2</sup> Ber. d. chem. Ges., 4, 707.

striking. It starts up almost as well as some others, but gets flatter and flatter and approaches, as a limit, the 50 per cent line instead of the 100 per cent line. This led to a long series of experiments in which the heating was continued for much longer periods in order to trace the curve to its limit. The velocity is seen to slow down as 50 per cent decomposition is approached. Five hours gave 45.6 per cent; six hours, 48.6 per cent; seven hours, 48.3 per cent; eight hours, 50.1 per cent; and fifteen hours only 49.7 per cent, while twenty-five hours gave 48.8 per cent. The figure for eight hours is probably a little too high. Those for seven and twenty-five hours are too low, the deficiency, especially in the latter, being probably due to a slight escape of the ammonia from the little flask during the long heating. It is difficult to get rubber stoppers to remain tight at 100° C. Both had to be heated for several successive laboratory days. From the results given, it seems that orthonitrobenzamide, when boiled with baryta water, gives up half of the calculated amount of ammonia, and that prolonged boiling does not increase this amount. The results for the last series of experiments with orthonitrobenzamide were calculated by considering that there were just half as many molecules of the amide as were actually put in, that is  $k$  is put equal to

$$\log \frac{(A-2x)\frac{1}{2}B}{(B-2x)A} = \frac{2.3025}{(A-\frac{1}{2}B)t}.$$

After the first hour this gives a very satisfactory value for  $k$  which remains nearly constant until nearly 50 per cent is reached. These results led to a somewhat more thorough study of this reaction. The alkaline solution of the amide rapidly becomes red on heating until in a short time it assumes a beautiful clear red color. On acidifying the red solution, in which the reaction had been pushed to the limit, it takes on a yellowish turbid condition and a brilliant red, flaky precipitate is formed. This collects at the bottom and is inclined to assume a somewhat tarry condition. It is easily soluble in alkali, from which it can be again precipitated by acid. It is readily soluble in alcohol





and comes down on the addition of water. If the alcoholic solution is allowed to evaporate, the substance is left as bright-red drops which on long standing solidify and then seem, when crushed, to be a mass of clear garnet-red crystals. I have obtained what seems to be the same substance by using caustic soda instead of baryta water. With caustic soda, containing even half a gram of hydrate to the cubic centimeter, it is impossible to get off more than half of the calculated ammonia even when boiled all day. With the most concentrated solutions, even less than half seems to come off, and the red substance, when precipitated, does not seem to be so pure as it does not so readily solidify. These facts are of interest as showing that at least one amide does not go into the corresponding acid when boiled with alkali. It is intended to investigate the red substance further.<sup>1</sup>

Many of the results here recorded are brought together at the end in the form of curves. The strange behavior of the *o*-nitrobenzamide is easily seen from an inspection of these. The form of the *o*-nitro curve is remarkable. It will be noticed that it crosses several of the others at quite sharp angles and approaches the 50 per cent line as an asymptote. At twenty-five hours or nearly three times the length of the curve as drawn, it is still only 50 per cent.

COLLEGE OF CHARLESTON,  
CHARLESTON, S. C.,  
June 25, 1900.

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Contributions from the Sheffield Laboratory of Yale University.

LXXVII.—ON THE MOLECULAR REARRANGEMENT OF DISUBSTITUTED THIONCARBAMIC ESTERS: PHENYLIMIDOTHIOCARBONIC ACID DERIVATIVES AND THIOSEMICARBAZIDIC ESTERS.

BY HENRY L. WHEELER AND GUY K. DUSTIN.

In previous articles from this laboratory it has been shown that monosubstituted thioncarbamic esters,  $\text{XNHCS.OH}$ , react more or less readily with alkyl iodides, giving the isomeric

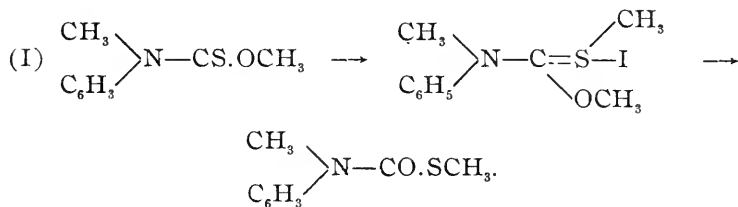
<sup>1</sup> Recent work has shown the red substance to contain some *o*-nitrobenzoic acid and another acid melting at about 261° C.

thiol derivatives,  $\text{XNHCO.SR}$ ; and it was concluded that these ester amides are best represented by the normal form

rather than by the pseudo structure,  $\text{XN}=\text{C} \begin{smallmatrix} \text{SH} \\ \text{OR} \end{smallmatrix}$ . It

seemed desirable, however, to determine whether or not the above-mentioned rearrangements were dependent on the presence of hydrogen; or, in other words, whether disubstituted xanthogenamides of the form  $\text{XX}'\text{N}-\text{CS.OR}$  would undergo a similar rearrangement, giving the thiol derivatives, the question being all the more interesting since it is customary to represent the thioamides and thioureas as reacting in their pseudoform with halogen compounds.

We find that the disubstituted thioncarbamic esters readily react with alkyl iodides, and that the N-methyl (I) and ethylthioncarbamic esters undergo a rearrangement even more readily than the thioncarbamic esters of the form  $\text{C}_6\text{H}_5\text{NHCS.OR}$ . It follows, therefore, that the pseudoform is not involved in these reactions, and that the rearrangement takes place, in general, as follows:

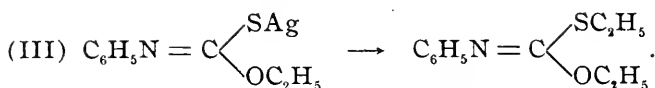


It is easy to distinguish whether a rearrangement has taken place or is complete in this series, since the thion derivatives are readily desulphurized by mercuric oxide when boiled in alcoholic solution, while the thiol derivatives are unaffected. The action takes place smoothly as follows:



It was shown by Liebermann<sup>1</sup> that the sodium and silver salts of the thioncarbamic esters react with alkyl halides in the following manner:

<sup>1</sup> Ann. Chem. (Liebig), **207**, 148.



Thus, the alkyl group attaches itself to sulphur and phenylimidothiocarbonic esters result. He examined the action of these compounds with sulphuric acid, aniline, and ammonia, at high temperatures. He found that the action of sulphuric acid gave aniline sulphate and thiocarbonic esters, thus showing the constitution of the compounds. With aniline, mercaptan was given off and carbanilide separated, while with ammonia (at  $100^\circ$ ) decomposition products alone were obtained. He states that with hydrochloric acid alkyl chloride is evolved, on warming, and the compounds are converted back into phenylsulphurethane.

We have prepared some of these compounds in order to compare their behavior with that of the analogous acylimido-

thiocarbonic esters,  $\text{C}_6\text{H}_5\text{CO}-\text{N}=\text{C} \begin{array}{l} \text{SC}_2\text{H}_5 \\ \text{OC}_2\text{H}_5 \end{array}$ , and with that of anilinoimidothiocarbonic ester, the hydrazone of diethyl thiocarbonate,  $\text{C}_6\text{H}_5\text{NH}-\text{N}=\text{C} \begin{array}{l} \text{SC}_2\text{H}_5 \\ \text{OC}_2\text{H}_5 \end{array}$ . The results of the

comparison show how strikingly the properties of compounds of similar structure are influenced by the character of groups.

It has been found that the benzoylimidothiocarbonic esters readily react with organic bases<sup>1</sup> while the hydrazone of ethyl thiocarbonate, which has precisely opposite properties, readily and smoothly reacts only with negative compounds, such as acyl chlorides, hydrochloric acid, thiobenzoic acid, etc.<sup>2</sup> We now find that the phenylimidothiocarbonic esters exhibit a behavior intermediate between the above, inasmuch as they are surprisingly unreactive with both acyl chlorides and with organic bases; in fact, they show a wide departure from most compounds which contain the imidoester grouping.

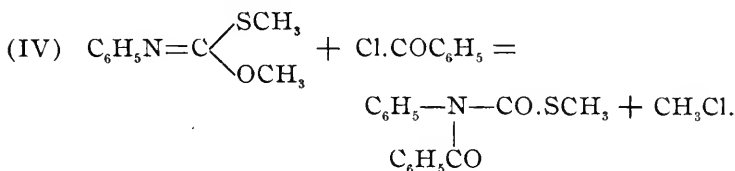
For example, it might be expected that the compounds of Liebermann would react with bases, giving the pseudourea

<sup>1</sup> Wheeler and Johnson: *This JOURNAL*, **24**, 189.

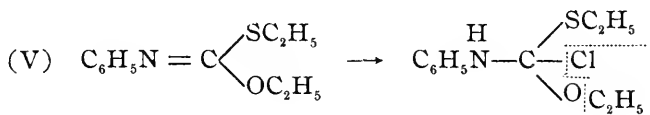
<sup>2</sup> Wheeler and Barnes: *Ibid.*, **24**, 60.

ethers of Stieglitz and Dains.<sup>1</sup> It was found, however, that aniline acts on these compounds only near its boiling-point, and then very slowly, and that carbanilide separates from the hot mixture, in crystalline form, before one-half of the mixture enters into reaction. On distilling, no pseudourea ether was found.

The hydrazone of thioethyl carbonate, like the isoanilides in general, reacts with acetyl and benzoyl chloride, in the cold with a violent evolution of alkyl chloride, while the compounds of Liebermann can be mixed with these chlorides without any evidence of reaction. Benzoyl chloride showed no signs of reacting with the following ester below 140°. On long continued heating, above this temperature, methyl chloride was slowly evolved and a benzoyl derivative was obtained. The reaction, in all probability, took place as follows :



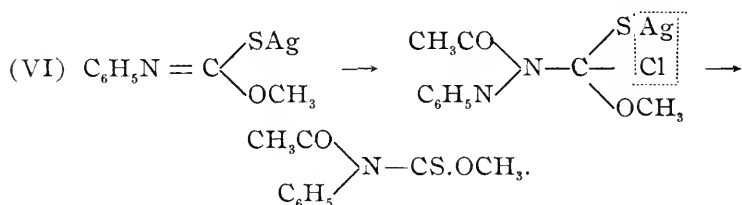
This action is probably analogous to that of hydrogen chloride, with which reagent the phenylimidothiocarbonic esters react smoothly and quantitatively, like the imidothiocarbonic esters in general, giving thiolcarbamic esters and not, as Lieberman states, regenerating phenylsulphurethane or the thion derivative. This mistake of Liebermann is probably due to the fact that ethyl thioncarbanilate and the corresponding thiol compound differ by about 1° in their melting-points, and may be easily mistaken for each other. However, the other members of these series differ more widely in their melting-points. The reaction with hydrogen chloride takes place with the formation of an addition-product, which decomposes with loss of alkyl chloride, as follows :



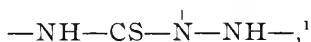
<sup>1</sup> J. Am. Chem. Soc., 21, 136.

In these and similar compounds it is almost invariably the group attached to oxygen that is evolved as alkyl chloride, and a thiol ester is formed. As another example of the comparative inertness of the phenylimidothiocarbonic acid grouping, we may add that no reaction was observed when benzoyl chloride was mixed with the silver salt of methyl thioncarbanilate suspended in benzene; and when the mixture was heated to  $100^\circ$  benzanilide was obtained.

With acetyl chloride the salt reacts in the cold. Silver chloride and an acetyl derivative are obtained as follows:



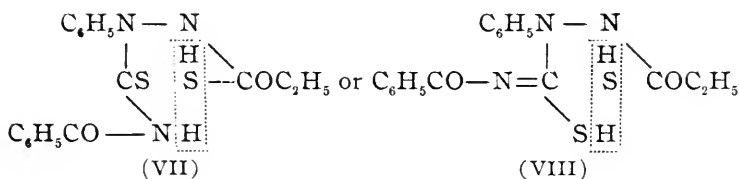
With the object of obtaining a new type of thiocarbamic esters, which perhaps may be called acylsulphosemicarbazidic esters, *i. e.*  $\text{C}_6\text{H}_5\text{CONHCSN}(\text{C}_6\text{H}_5)-\text{NHCSOR}$ , etc., since they contain the sulphosemicarbazide grouping,



we examined the behavior of acetyl and benzoylsulphocyanides with ethyl phenylthiocarbazinates. It was found that the thion ester behaves in a different manner from that of the thiol ester.

When acetyl- or benzoylsulphocyanide is mixed with ethyl phenylthioncarbazinate, hydrogen sulphide is evolved, even in the cold, and compounds of a very stable nature result. The reaction evidently takes place first by addition, with the formation of ethyl *c*-benzoyl-*b*-phenylsulpho-*a*-thionsemicarbazidate. This probably takes place according to one of the two following schemes, and hydrogen sulphide then separates as shown by the dotted lines, giving ring-formed compounds which are either triazole (VII) or thiobiazolone derivatives (VIII):

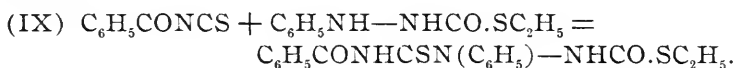
<sup>1</sup> For convenience in naming these compounds, sulphur in the urea radical is termed sulpho; when in the ester grouping it is called thion or thiol; and for general reference the compounds are referred to as thiosemicarbazidic esters.



Which ring is formed depends on whether the intermediate addition-product has the structure of a normal (VII) or pseudosulpho (VIII) semicarbazidic ester.

Freund and König<sup>1</sup> represent the action of isocyanophenyl chloride,  $\text{C}_6\text{H}_5\text{N}=\text{CCl}_2$ , on acylhydrazines in the same manner as that of phosgene, the products being viewed as imidoxybiazolines or compounds analogous to (VIII). The action in the present case might be expected to be similar. On the other hand, it has been shown by Marckwald<sup>2</sup> that compounds of this type are not desulphurized by metallic oxides while our material is desulphurized by silver nitrate; therefore, at present, we are inclined to represent these compounds as triazole derivatives, and assume the action to proceed as shown in (VII).

When acetyl- or benzoylsulphocyanide is mixed with ethyl phenylthiolcarbazinate no hydrogen sulphide is evolved, but the compounds unite directly to form an addition-product, as follows :



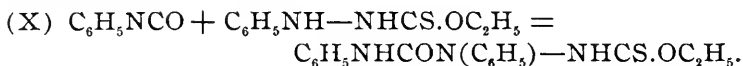
These reactions sharply distinguish the thion- from the thiolcarbazinic esters, and the ease with which the former give ring compounds seems to indicate that the thion derivatives have the pseudo form. However, other facts, such as special arrangement, must also be considered in these cases.

That the above formation of triazole derivatives (VII) is probably not caused by the phenylthioncarbazinic ester having the pseudo form is shown by the behavior of the latter with phenyl isocyanate. These compounds combine directly without giving off hydrogen sulphide, and the product has the

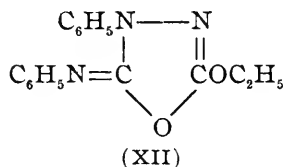
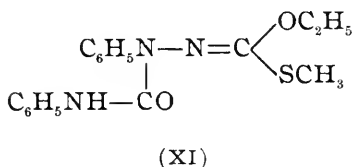
<sup>1</sup> Ber. d. chem. Ges., **26**, 2869.

<sup>2</sup> *Ibid.*, **25**, 3109; **27**, 617.

composition of the expected ethyl *c,b*-diphenyl-*a*-thionsemicarbazidate :

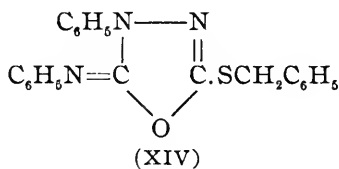
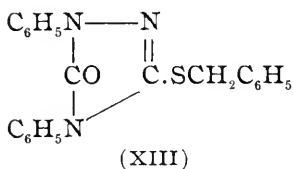


That the addition takes place to the nitrogen to which the phenyl group is attached, and that the grouping  $-NHCS.OC_2H_5$  is present, is shown by the behavior of the compound with alkali and alkyl iodides. With methyl iodide and sodium methylate in the cold, diphenylureaimidothiolmethyl-ethylcarbonate, the diphenylsemicarbazone of thioldmethyl-ethylcarbonate, is formed (XI) ; while under the same conditions ethyl iodide gives a mixture of two compounds. These are thioldiethylcarbonicesterdiphenylsemicarbazone analogous to (XI) and a substance, free from sulphur, which appears to be the ring-formed compound  $\alpha$ -ethoxy- $\alpha'$ -phenylimido- $\beta'$ -phenyloxybiazoline (XII) :



The compound (XII) is also formed on simply warming the diphenylthionsemicarbazidic ester with sodium ethylate.

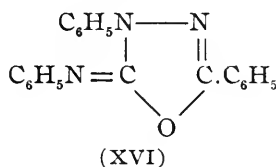
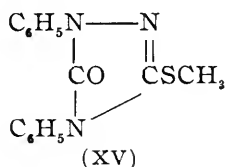
On the other hand, with benzyl chloride the sole product obtained was not strictly analogous to either of the above derivatives ; it contained sulphur and agreed in composition with one of the following compounds :



At present we have nothing but the properties of the compound to indicate to which of these series it belongs. The structure represented by formula (XIII) appears to be ex-



cluded, since Marckwald<sup>1</sup> has prepared a compound of this type, namely, 1,4-diphenyltriazolone-3-methylmercaptan (XV), and he has shown that this substance has decided basic properties, that it is soluble in acids, and that it gives a platinum double salt. Our compound, on the other hand, has no basic properties whatever. The nearest known analogues of a compound represented by formula (XIV) are the phenylimidooxybiazolines prepared by Freund and König<sup>2</sup>. The properties of their "*n*-phenyl-phenyl-phenylimidooxybiazolin" ( $\alpha$ -phenyl- $\alpha'$ -phenylimido- $\beta$ -phenyloxybiazoline, XVI) are closely similar to those of our compound, inasmuch as it is insoluble in water and is not affected by boiling with soda or hydrochloric acid, in which it is also insoluble :



Moreover, it was found that the compound free from sulphur, mentioned above, has no basic properties, and therefore it appears that formulæ (XII) and (XIV) best represent the structure of the compounds in question. Further work on the structure of these compounds must be deferred to a later date, owing to the departure of one of us from this laboratory.

The behavior of the diphenylthionsemicarbazidic ester (X) with bases showed a wide departure from that of the benzoylthioncarbamic esters since derivatives of a pseudourea type were not obtained. When heated with aniline, or in fact when heated alone, carbanilide is the chief product. The properties of this type of esters are most closely related to those of the thioncarbanilic esters.

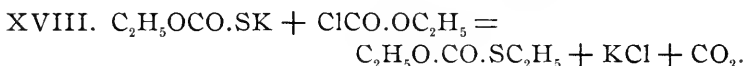
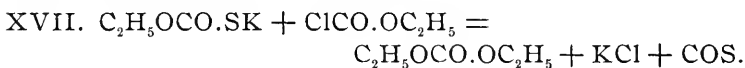
When the diphenylsemicarbazones of the thiocarbonic esters (XI) are treated with hydrogen chloride, a reaction similar to that described in the case of the phenylimidothiocarbonic esters takes place (V above). The compounds obtained are identical with those prepared by adding phenyl isocyanate to

<sup>1</sup> Ber. d. chem. Ges., 25, 3111.

<sup>2</sup> Loc. cit.

the phenylthiolcarbazonic esters, in which case again no hydrogen sulphide is evolved; the addition therefore takes place in a similar manner to that shown in (X).

In addition to the above we have investigated the action of some thion and thiol salts of carbonic and carbamic acids with ethyl chlorcarbonate, and we find that no two of these salts behave alike. For example, Bender's salt, to which the structure  $C_2H_5OCO.SK$  is assigned, reacts in two ways as follows, chiefly according to (XVII) :



The products are diethyl carbonate, diethyl thiolcarbonate, carbon oxysulphide, carbon dioxide, and potassium chloride.

Potassium xanthate,  $C_2H_5OCS.SK$ , reacts with 1 molecule of chlorcarbonic ester in an extremely complicated manner. We identified the presence of five different oils in the reaction-product. These were carbon disulphide, ethyl carbonate, diethyl thioncarbonate, xanthogenic ester, and Welde's<sup>1</sup> "disulphodicarbothionsäurediäthyl ester."

We were unable to obtain the sodium salt of thionethylcarbonate,  $C_2H_5OCS.ONa$ , described by Klason.<sup>2</sup> In this respect our experience coincides with that of Bergreen,<sup>3</sup> whose results on the action of thiophosgene on sodium ethylate we are able to confirm.

Ammonium dithiocarbanilate,  $C_6H_5NHCS.SNH_4$ , gave, with 1 molecule of chlorcarbonic ester, chiefly thiocarbanilide, phenylsulphocarbamide, and phenyl mustard oil; while the phenylhydrazine salt of dithiophenylcarbazonic acid,



gave a good yield of Heller's<sup>4</sup> ethyl phenylcarbazonate. The

<sup>1</sup> J. prakt. Chem. [2], 15, 45.

<sup>2</sup> Ber. d. chem. Ges., 20, 2384.

<sup>3</sup> *Ibid.*, 21, 346.

<sup>4</sup> Ann. Chem. (Liebig), 263, 278.

latter had all the properties mentioned by Widman.<sup>1</sup> Besides this an unpromising green tar was formed.

## EXPERIMENTAL PART.

*Methyl Methylthioncarbanilate*,  $\begin{array}{c} \text{CH}_3 \\ \text{C}_6\text{H}_5 \end{array} \text{N} - \text{CS} \cdot \text{OCH}_3$ . — The

chloride,  $\text{C}_6\text{H}_5(\text{CH}_3)\text{NCS} \cdot \text{Cl}$ , was prepared by the method of Billeter.<sup>2</sup> In two experiments 15 grams of thiophosgene gave the theoretical yield of the chloride. This was added to a solution of sodium methylate in methyl alcohol when a reaction took place at once; it was warmed for a half hour on the water-bath, then treated with water, extracted with ether, and distilled at 19 mm. pressure, whereupon it boiled mostly from 151°–152°. It was a colorless oil which did not solidify on cooling, and a nitrogen determination gave:

	Calculated for $\text{C}_9\text{H}_{11}\text{NOS}$ .	Found.
N	7.7	7.3

*Methyl Methylcarbanilate*,  $\text{C}_6\text{H}_5(\text{CH}_3)\text{NCO} \cdot \text{OCH}_3$ , was formed on boiling the above thion ester (12 grams) with an excess of mercuric oxide in alcoholic solution. It was obtained as an oil which distilled for the most part from 117° to 119° at 16 mm. pressure, and a nitrogen determination gave:

	Calculated for $\text{C}_9\text{H}_{11}\text{NO}_2$ .	Found.
N	8.48	8.71

*Ethyl Methylthioncarbanilate*,  $\text{C}_6\text{H}_5(\text{CH}_3)\text{NCS} \cdot \text{OC}_2\text{H}_5$ . — This was prepared from the above chloride in the same manner as the methyl ester. It formed a colorless oil which boiled mostly from 145° to 150° at 18 mm. pressure. It refused to solidify, and a nitrogen determination gave:

	Calculated for $\text{C}_{10}\text{H}_{13}\text{NOS}$ .	Found.
N	7.1	6.9

It may be boiled with concentrated hydrochloric acid without change.

<sup>1</sup> Ber. d. chem. Ges., 28, 1927.

<sup>2</sup> Ibid., 20, 1631.

*Methyl N-Ethylthioncarbanilate*,  $C_6H_5(C_2H_5)NCS.OCH_3$ .—This compound was prepared in the same manner as the corresponding ethyl ester.<sup>1</sup> The crude product was obtained as an oil which was distilled at 18 mm. pressure, whereupon the most of the material boiled from 148° to 149°. It then solidified and, on crystallizing from petroleum ether, beautiful, colorless, five-sided plates separated, melting from 41° to 42°. A nitrogen determination gave :

	Calculated for $C_{10}H_{13}NOS$ .	Found.
N	7.17	7.50

*Methyl Methylthiolcarbanilate*,  $C_6H_5(CH_3)NCO.SCH_3$ .—This compound is easily obtained when the thion ester is heated with methyl iodide for four hours from 103° to 106°. On cooling, a small amount of crystalline material separates, which appears to be trimethylphenylammonium iodide. The rest of the product, when distilled at 16 mm. pressure, boils for the most part from 140° to 142°. The material then solidifies, and when crystallized from alcohol, in which it is readily soluble, it melts at 46°. It forms colorless plates which, on analysis, gave :

	Calculated for $C_9H_{11}NOS$ .	Found.
N	7.77	7.38

This ester has been obtained in another manner by Bertram.<sup>2</sup> He states that it melts at 54°. Our material was free from the thion ester since it was not desulphurized on boiling with mercuric oxide.

*Ethyl N-Methylthiolcarbanilate*,  $C_6H_5(CH_3)NCO.SC_2H_5$ .—The thion ester was heated in a closed tube for a number of hours at 100° with ethyl iodide, then, on distilling, an oil was obtained which boiled from 160° to 163° at 19 mm. pressure. On cooling, this solidified and melted from about 12°–13°. A nitrogen determination gave :

	Calculated for $C_{10}H_{13}NOS$ .	Found.
N	7.17	7.38

<sup>1</sup> Billeter and Strohl : Ber. d. chem. Ges., 21, 104.

<sup>2</sup> Ber. d. chem. Ges., 25, 53.

*Methyl N-Ethylthiolcarbanilate*,  $C_6H_5(C_2H_5)NCOSCH_3$ . — This was obtained as an oil by heating the thion ester with methyl iodide. It boiled from  $148^\circ$  to  $149^\circ$  at 17 mm. pressure, and it did not solidify on cooling. A nitrogen determination gave results agreeing with the calculated. The record of this determination is lost. It was free from the thion ester, since it was not desulphurized by boiling in alcoholic solution with mercuric oxide.

*Ethyl N-Dimethylthioncarbamate*,  $(CH_3)_2NCS.OC_2H_5$ . — The action of alcoholic dimethylamine was tried on xanthogenic ester in order to see if the action in the case of aliphatic amines is the same as that of ammonia and phenylhydrazine. It was found that these substances react less smoothly than when ammonia is used. In the present case, after the above mixture was allowed to stand about two weeks, the product was an oil which distilled, for the most part, at  $203^\circ$ – $205^\circ$ . A nitrogen determination indicated the presence of xanthogenic ester. The material was then treated with alcoholic potash and allowed to stand for twenty-four hours, whereupon, on distilling, it boiled from  $205^\circ$  to  $206^\circ$ , and a nitrogen determination gave 9.1 per cent of nitrogen instead of 10.5.

Diamylamine reacted even less smoothly with xanthogenic ester. When these substances were mixed and allowed to stand for four or five days, then heated for some time on the steam-bath, mercaptan was given off, but the product, when distilled, gave no constant boiling-point.

*Dimethyl Phenylimidothiolcarbonate*,  $C_6H_5N=C \begin{matrix} \diagup SCH_3 \\ \diagdown OCH_3 \end{matrix}$ . —

This was prepared by treating methyl thioncarbanilate in methyl alcohol with sodium methylate and methyl iodide. On distilling, the product boiled at  $133^\circ$  at 17 mm. pressure and was a yellow oil with a peculiar odor. When this was treated with hydrogen chloride in solution in benzene, no precipitate was obtained, the solution evolved heat, and methyl chloride escaped. On evaporation, an oil was obtained which solidified to a mass of colorless crystals, and when crystallized from petroleum ether, fine, long needles were obtained, melting from  $83^\circ$  to  $84^\circ$ . This material was identical in every re-

spect with *methyl thiolcarbanilate*,  $C_6H_5NHCO.SCH_3$ . The thion ester melts at  $97^\circ$ .<sup>1</sup>

When the above imidothiolcarbonic ester was heated with aniline in an oil-bath at  $180^\circ$ – $190^\circ$  for several hours, carbanilide crystallized out from the hot mixture. The heating was then stopped and the mass filtered and the oil distilled at 17 mm. pressure, whereupon about one-half of the product boiled from  $82^\circ$ – $131^\circ$ , and the remainder from  $131^\circ$ – $140^\circ$ . It follows from this that little or no methylisocarbanilide was present, since the isourea ethers boil near  $200^\circ$  at the above pressure.<sup>2</sup> On heating this carbonic ester derivative with diisobutylamine for several hours in an oil-bath from  $145^\circ$ – $150^\circ$  no effervescence took place and little or no mercaptan was evolved. This deportment with bases is in striking contrast with the behavior of the benzoylimidothiocarbonic acid derivatives which readily react at a much lower temperature.<sup>3</sup>

*Methyl Benzoylthiolcarbanilate*,  $C_6H_5CO(C_6H_5)N-CO.SCH_3$ .—On mixing 2 grams of the above dimethyl carbonate with 1 molecular proportion of benzoyl chloride and heating, no action was observed below  $140^\circ$ . At this temperature methyl chloride was evolved, and on maintaining the bath at  $150^\circ$  for several hours a slow evolution of gas was noticed. On cooling and crystallizing the residue from petroleum ether, well-crystallized needles or prisms were obtained melting at about  $93^\circ$ . When this was mixed with methyl thioncarbanilate (melting-point  $97^\circ$ ) the mixture melted at about  $83^\circ$ . A nitrogen determination gave :

	Calculated for $C_{16}H_{13}NO_2S$ .	Found.
N	5.16	5.75

That this material is a benzoyl derivative was shown by warming it with aniline on the water-bath when benzanilide was obtained.

When dimethyl phenylimidothiolcarbonate was mixed with acetyl chloride no action whatever was observed, while the analogous ethyl phenylimidoformate,  $C_6H_5N=CHOC_2H_5$ , reacts violently with acetyl chloride.<sup>4</sup>

<sup>1</sup> Orndorff and Richmond: This JOURNAL, 22, 462.

<sup>2</sup> Stieglitz, also Dains: *Loc. cit.*

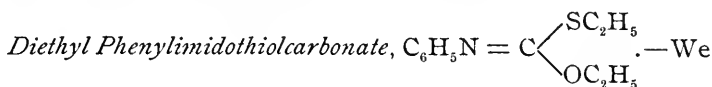
<sup>3</sup> Wheeler and Johnson: This JOURNAL, *loc. cit.*

<sup>4</sup> Wheeler and Walden: This JOURNAL, 19, 134.

*Methyl Acetylthioncarbanilate*,  $\text{CH}_3\text{CO} \cdot (\text{C}_6\text{H}_5)\text{NCS} \cdot \text{OCH}_3$ .—The silver salt of methyl thioncarbanilate was prepared in the usual way by means of sodium hydrate and alcoholic silver nitrate. It forms an amorphous gray precipitate. When this (17 grams), after drying, was treated with acetyl chloride in benzene, a reaction took place in the cold, and on evaporating the benzene and crystallizing the residue from dilute alcohol, colorless crystals separated melting from  $47^\circ$ – $49^\circ$ . A nitrogen determination gave :

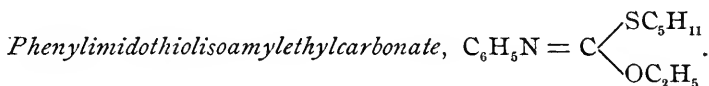
	Calculated for $\text{C}_{10}\text{H}_{11}\text{NO}_2\text{S}$ .	Found.
N	6.69	6.71

The material was desulphurized on boiling in alcoholic solution with mercuric oxide, showing the presence of the thion group. When this compound was warmed with aniline it gave methyl thioncarbanilate and acetanilide.



prepared this ester according to the directions of Liebermann<sup>1</sup> except that alcoholic solutions were used instead of aqueous, as otherwise it frequently happens that a product is obtained which is completely decomposed when distilled. This ester was found to boil from  $157^\circ$ – $160^\circ$  at 21 mm. pressure.

When this oil was treated with hydrogen chloride in benzene no precipitate was obtained. On evaporating and crystallizing the residue from dilute alcohol, needles separated which melted at about  $69^\circ$ . That this material was ethyl thiolcarbanilate and not the thion compound was shown by mixing a portion with each of these substances. When mixed with the thiol ester melting from  $69^\circ$ – $70^\circ$  the mixture melted unaltered at the same temperature ; when mixed with the thion ester melting at about  $71^\circ$  it melted below  $60^\circ$ .



—This oil was prepared by Mr. T. B. Johnson in order to compare its behavior towards hydrogen chloride with that of

<sup>1</sup> Ann. Chem. (Liebig), **207**, 150.

the analogous compound,  $\text{C}_6\text{H}_5\text{CON}=\text{C} \begin{cases} \text{SC}_5\text{H}_{11} \\ \text{OC}_2\text{H}_5 \end{cases}$ , which later gives a thion and not the thiol ester. The oil was made by treating the sodium salt of ethyl thioncarbanilate in alcohol with amyl bromide. When the mixture no longer gave an alkaline reaction, water was added, and the product extracted with ether. On attempting to distil the oil under reduced pressure it decomposed. A portion of the crude material was saturated in benzene with hydrogen chloride, whereupon, on evaporating and crystallizing the residue from alcohol, long, colorless needles were obtained which melted at  $66^\circ$  and had all the properties of isoamyl thiolcarbanilate.

*Action of Acetyl rhodanide on Ethyl Phenylthioncarbazinate.*—Two grams of the latter and 1 gram of the former were mixed together and gently warmed, whereupon hydrogen sulphide was evolved; when this ceased and the product was crystallized from 95 per cent alcohol bunches of colorless needles separated, which melted from  $93^\circ$ – $94^\circ$ . A nitrogen determination gave the following result:

	Calculated for $\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}_2\text{S}$ .	Found.
N	15.96	16.54

For reasons stated in the introduction, this product is in all probability 1-phenyl-3-ethoxy-4-acetyl-5-sulphotriazolone.

*Action of Benzoyl rhodanide on Ethyl Phenylthioncarbazinate.*—Two grams of the carbazinic ester were mixed with 1.4 grams of the rhodanide and warmed, after hydrogen sulphide ceased being evolved, the product was crystallized from alcohol, whereupon flattened prisms melting from  $136^\circ$ – $138^\circ$  were obtained. These, on analysis, gave:

	Calculated for $\text{C}_{17}\text{H}_{15}\text{N}_3\text{O}_2\text{S}$ .	Found.
N	12.9	12.6

The analytical result agrees with the calculated for 1-phenyl-3-ethoxy-4-benzoyl-5-sulphotriazolone. This compound is exceedingly stable, since it was found that it can be boiled with hydrochloric acid, concentrated ammonia, strong potash, aniline; and also with benzoyl chloride and be recovered un-



altered. An alcoholic solution of silver nitrate desulphurizes it on boiling, which fact indicates that the substance is a triazole derivative and not a biazolone.

*c-Acetylsulpho-b-phenyl-a-semicarbazidichiolethyl Ester*,  
 $\text{CH}_3\text{CONH}-\text{CS}-\text{N}(\text{C}_6\text{H}_5)-\text{NHCO}.\text{SC}_2\text{H}_5$ .—When 1 gram of thiolphenylcarbazine ethyl ester was mixed with 0.5 gram of acetylthionamide in benzene solution and the whole was warmed, no hydrogen sulphide was noticeable. On standing, long prisms separated, melting at  $145^\circ$ . These were difficultly soluble in benzene, and an analysis gave :

	Calculated for $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_2\text{S}_2$ .	Found.
N	14.14	14.28

When this product is heated to  $160^\circ$ , mercaptan is evolved.

*c-Benzoylsulpho-b-phenyl-a-semicarbazidichiolethyl Ester*,  
 $\text{C}_6\text{H}_5\text{CONH}-\text{CS}-\text{N}(\text{C}_6\text{H}_5)-\text{NHCO}.\text{SC}_2\text{H}_5$ .—Benzoylthionamide and ethyl thiolphenylcarbazine readily combine in benzene solution. The product separates from benzene in colorless needles or prisms melting at  $148^\circ$ – $150^\circ$ . A nitrogen determination gave :

	Calculated for $\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2\text{S}_2$ .	Found.
N	11.69	12.13

*c,b-Diphenyl-a-semicarbazidichionethyl Ester*,  
 $\text{C}_6\text{H}_5\text{NH}-\text{CO}-\text{N}(\text{C}_6\text{H}_5)-\text{NHCS}.\text{OC}_2\text{H}_5$ .—Ethyl thionphenylcarbazine dissolves in the calculated quantity of phenyl isocyanate, when the mixture is gently warmed, and then solidifies. On crystallizing the material then from alcohol colorless prisms, melting from  $114^\circ$ – $115^\circ$ , separate. Nitrogen determinations gave the following results :

	Calculated for $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_2\text{S}$ .	I.	Found.	II.
N	13.0	13.09		13.01

When this material was heated with aniline, carbanilide was obtained which was identified by its properties and also by a nitrogen determination.

*c,b-Diphenyl-a-semicarbazidichiolethyl Ester*,  
 $\text{C}_6\text{H}_5\text{NH}-\text{CO}-\text{N}(\text{C}_6\text{H}_5)-\text{NHCO}.\text{SC}_2\text{H}_5$ , formed by adding phenyl isocyanate to the thiolcarbazine ester, crystallizes in

small, spear-shaped plates, which are quite difficultly soluble in alcohol and which melt at  $156^{\circ}$ . A nitrogen determination gave :

	Calculated for $C_{16}H_{17}N_3O_2S$ .	Found.
N	13.0	13.2

These esters are soluble in alkali and on boiling are decomposed.

*c, b-Diphenyl-a-semicarbazidictiomethyl Ester*,  
 $C_6H_5NHCO-N(C_6H_5)-NHCO.SCH_3$ .—This was prepared in a similar manner to the above ethyl ester in order to determine whether it could be converted into the "diphenylimidobiazolonyl- $\mu$ -methylsulfid," (1,4-diphenyltriazolone-3-methylmercaptan of Marckwald),<sup>1</sup> the nearest analogue of the ring-formed compounds described in this paper, and thus decide whether the compounds in question are triazol derivatives or thiobiazolones. Theoretically, all that is required is the removal of water from the above ester in the same manner as hydrogen sulphide separates in formula VII, but attempts to do this were without success. The ester crystallizes from alcohol in small plates, which melt at  $186^{\circ}$ , and it is identical with the compound prepared from diphenylureaimidothiol-methylethylcarbonate (see below) and hydrogen chloride. When heated to its melting-point it decomposes, slowly giving off mercaptan and phenyl isocyanate. It dissolves in concentrated sulphuric acid and is precipitated unaltered by water. It can be boiled with acetic anhydride, from which it crystallizes unaltered in prisms. It is insoluble in concentrated boiling hydrochloric acid, but it dissolves readily in alkali. When the alkaline solution was boiled an inflammable gas was given off and, on cooling, needles separated. These melted at  $161^{\circ}$ , after crystallization from alcohol, and were insoluble in hydrochloric acid. This was not the compound sought for, and therefore it was not further examined.

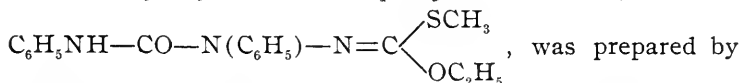
*c, b-Diphenyl-a-semicarbazidictiolbenzyl Ester*,  
 $C_6H_5NHCO-N(C_6H_5)-NHCO.SCH_2C_6H_5$ .—Phenyl isocyanate unites readily with thiolphenylcarbazinicbenzyl ester in benzene solution. The product is readily soluble in benzene

<sup>1</sup> Ber. d. chem. Ges., 25, 3111.

and hot alcohol, difficultly soluble in cold alcohol, and insoluble in water. It crystallizes in small bunches of flattened prisms or plates, which melt at about  $150^{\circ}$ . A nitrogen determination gave :

	Calculated for $C_{21}H_{19}N_3O_2S$ .	Found.
N	11.1	10.8

*Thiolmethylethylcarbonicesterdiphenylsemicarbazone*,

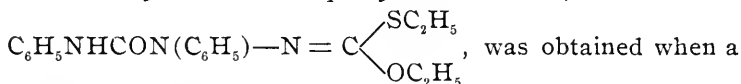


adding ice-cold sodium methylate and methyl iodide to the above diphenylsemicarbazidichionethyl ester. After remaining in the cold for two hours the action was complete, whereupon water was added, and the product extracted with ether. On crystallizing from alcohol, lozenge-shaped crystals were obtained which melted at  $108^{\circ}$ – $109^{\circ}$ , and a nitrogen determination gave :

	Calculated for $C_{17}H_{19}N_3O_2S$ .	Found.
N	12.7	12.6

When this substance, dissolved in benzene, was treated with hydrogen chloride, ethyl chloride was evolved and the above-described thiolmethyl ester, which melts at  $186^{\circ}$ , was obtained.

*Thioldiethylcarbonicesterdiphenylsemicarbazone*,



mixture of ethyl bromide, sodium ethylate, and the above thionsemicarbazidicethyl ester was allowed to stand at ordinary temperatures for several hours. On crystallizing the product from dilute alcohol, needles were obtained which melted at about  $111^{\circ}$ . The yield is poor, as under these conditions a compound free from sulphur is also formed. The compound melting at  $111^{\circ}$  gives the above-described ethyl thiolsemicarbazidate with hydrogen chloride, a reaction which easily serves to identify it. It is readily soluble in alcohol and benzene, difficultly in petroleum ether, and insoluble in water.

*α-Ethoxy-α-phenylimido-β'-phenyloxybiazoline,*

$$\begin{array}{c} \text{C}_6\text{H}_5\text{N} \text{---} \text{N} \\ | \quad \quad \quad || \\ \text{C}_6\text{H}_5\text{N}=\text{C} \text{---} \text{O} \text{---} \text{COC}_2\text{H}_5 \end{array}$$
 .—This appears to be the compound free from sulphur that accompanies the above carbonic ester derivative. It was also obtained when 2 grams of *c,b*-diphenyl-*α*-semicarbazidichionethyl ester was boiled in alcohol with sodium ethylate for two hours. Water then precipitated the compound, which crystallized in fine, long, slender prisms from alcohol. It melted at 86°, and a nitrogen determination gave :

	Calculated for $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_2$ .	Found.
N	14.9	14.6

*α-Benzylmercapto-α'-phenylimido-β'-phenyloxybiazoline,*

$$\begin{array}{c} \text{C}_6\text{H}_5\text{N} \text{---} \text{N} \\ | \quad \quad \quad || \\ \text{C}_6\text{H}_5\text{N}=\text{C} \text{---} \text{O} \text{---} \text{CSCH}_2\text{C}_6\text{H}_5 \end{array}$$
 .—When the above diphenyl-semicarbazidichionethyl ester is dissolved in aqueous alkali and warmed with benzyl chloride, an oil is obtained which, on cooling, solidifies. On crystallizing from alcohol, the material separates in the form of colorless needles melting at 110°–112°. This contains sulphur, and nitrogen determinations gave :

	Calculated for $\text{C}_{21}\text{H}_{17}\text{N}_3\text{OS}$ .	I.	Found.	II.
N	11.6	11.5		11.5

This compound is insoluble in boiling water and hydrochloric acid, concentrated or dilute. It is insoluble and gives off no mercaptan on boiling with strong potash. The properties have nothing in common with Marckwald's 1,4-diphenyl-triazolone-3-methylmercaptan, and therefore they indicate that this compound is not a triazol derivative. When the substance is heated with phosphorus pentachloride hydrogen chloride is evolved, indicating decomposition.

*The Behavior of Bender's Salt,  $\text{C}_2\text{H}_5\text{OCO.SK}$ , with Ethyl Chlorcarbonate.*—When 55 grams of the salt were treated with the calculated quantity of ethyl chlorcarbonate, the latter being dropped slowly on the salt, an energetic reaction took place and carbon dioxide and carbon oxysulphide were

evolved. The latter was identified by standing over water when hydrogen sulphide was formed. On distilling the product it boiled from  $125^{\circ}$ – $217^{\circ}$ (?). The greater portion came over from  $125^{\circ}$ – $144^{\circ}$ ; this, when redistilled, gave 20 grams of oil boiling at about  $126^{\circ}$ , which proved to be ethyl carbonate. The higher-boiling portions gave urethane, carbamide, and mercaptan when treated with alcoholic ammonia, indicating the presence of thioethyl carbonate.

*Potassium Xanthate,  $C_2H_5OCS.SK$ , and Ethyl Chlorcarbonate.*—When 55 grams of potassium xanthate and 37 grams of ethyl chlorcarbonate were allowed to react and the gas that was evolved was passed into alcoholic potash, no test for carbon oxysulphide was obtained. It appeared to consist entirely or, at any rate for the most part, of carbon dioxide. On distilling the resulting oil, 5 grams boiling below  $161^{\circ}$ , 31 grams from  $161^{\circ}$ – $181^{\circ}$ , and 10 grams from  $181^{\circ}$ – $186^{\circ}$  were collected.

It was found on redistilling these fractions that they boiled through a much wider range and that no definite boiling-point could be obtained. In the first portions, carbon disulphide ( $45^{\circ}$ – $120^{\circ}$ ) and ethyl carbonate ( $126^{\circ}$ – $130^{\circ}$ ) were identified. On treating portions boiling from  $130^{\circ}$  to above  $200^{\circ}$  with alcoholic ammonia, ammonium sulphocyanide, ammonium carbonate, ammonium sulphide, and xanthogenamide were obtained, thus indicating the presence of thionethyl carbonate, xanthogenic ester, and Welde's<sup>1</sup> compound,  $S(CS.OC_2H_5)_2$ .

*Ammonium Dithiocarbanilate,  $C_6H_5NHCS.SNH_4$ , and Ethyl Chlorcarbonate.*—When the dry salt was treated with chlorcarbonic ester in molecular proportions, an energetic reaction took place, carbon oxysulphide was evolved, and a semisolid residue was obtained. On treating this with alkali and warming, little or nothing dissolved except ammonium chloride (absence of ethyl thioncarbanilate). The material had a strong odor of phenyl mustard oil, which was removed by treating with ether. On crystallizing from alcohol two substances were obtained, one melting at  $150^{\circ}$  (plates) which proved to be carbanilide, the other melting at  $154^{\circ}$  (prisms), which on analysis gave 18.2 per cent of nitrogen, while the calculated for monophenylthiourea is 18.4 per cent.

<sup>1</sup> *Loc. cit.*

The phenylhydrazine salt of dithiophenylcarbazinic acid and ethylchlorcarbonate react in benzene solution without evolution of gas. On filtering from phenylhydrazine hydrochloride, evaporating the benzene solution, and then crystallizing the residue from a mixture of benzene and petroleum ether, colorless prisms were obtained which melted from  $76^{\circ}$ – $77^{\circ}$ . A nitrogen determination gave :

N	Calculated for	Found.
	$C_6H_5NH-NHCO_2C_2H_5 \cdot H_2O$ .	
	14.1	14.5

The solution in sulphuric acid gave an intense red color with ferric chloride, the compound agreeing in properties with those described by Widman for ethyl phenylcarbazinate.

NEW HAVEN, CONN., May 14, 1900.

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Contribution from the Chemical Laboratory of the Massachusetts Institute of Technology.

## XXVI.—THE DETECTION OF METHYL ALCOHOL IN MIXTURES.

BY S. P. MULLIKEN AND HEYWARD SCUDDER.

In a recent article by E. Jandrier<sup>1</sup> it is stated that a test for methyl alcohol described by us<sup>2</sup> in an earlier number of this JOURNAL and based on the oxidation of the alcohol to formic aldehyde, followed by condensation of the latter to a colored derivative of resorcine, is unreliable, because it is also given by acrolein and is interfered with by the presence of furfurol. To remedy these defects in our method Jandrier recommends that gallic acid be employed instead of resorcine as the reagent for formic aldehyde, he having found in an earlier investigation<sup>3</sup> that the color reaction obtained by the use of gallic acid is much more delicate and less likely to be obscured by colorations occasioned by the simultaneous presence of other aldehydes.

A careful examination by the authors of this modification of their test soon proved that its use for the purpose proposed is entirely inadmissible, and this despite the fact that gallic

<sup>1</sup> Ann. Chim. Anal. App. 4, 156; Centrbl., 1899, I, 1296 (abstract).

<sup>2</sup> This JOURNAL, 21, 266.

<sup>3</sup> Barbier and Jandrier: Ann. Chim. Anal. App., 1, 325; Analyst, 21, 295 (abstract).

acid is actually, as claimed, a better reagent for the detection of formic aldehyde than is resorcine! The explanation of this paradox will be made apparent by a consideration of certain facts that have lately come to our knowledge while studying the partial oxidation by hot copper oxide of a considerable number of organic compounds.

The means chosen for oxidizing methyl alcohol to formic aldehyde detailed in our first paper, was the very simple one of plunging a short, closely-wound spiral of light copper wire, previously heated to redness and superficially oxidized, into the solution to be tested. Special emphasis was placed on the condition that "A concentrated spirit should always be diluted with at least three or four volumes of water before oxidation." It was also particularly noted that 1 drop of 0.5 per cent resorcine solution was the quantity of reagent that should be added for every 3 cc. of all solutions originally containing more than 0.1 per cent of methyl alcohol. These minute specifications were necessary, partly because it had been found that absolute ethyl alcohol, when directly oxidized without previous dilution, would, if afterwards largely diluted with water, give a very faint color reaction resembling that caused by formic aldehyde. This color was, however, noticed only when the weight of resorcine added to a given volume of solution was many times less than that usually employed, and it first made its appearance after several hours instead of within a few minutes, as usually happened with solutions that really contained methyl alcohol. The conditions necessary for the production of this color from ethyl alcohol were so unusual, its intensity was so slight, and its cause so obscure, that no account of it was included in our first paper. A more suggestive observation was made by us at the same time with reference to the use of caseine, of which we wrote:<sup>1</sup> "Caseine is not a suitable reagent for methyl alcohol tests, because the oxidation-products of ethyl alcohol yield with it the same blue color as formic aldehyde; though singularly enough solutions of pure acetaldehyde do not give this result."

After the gallic acid reaction for formic aldehyde had been brought to our attention, we endeavored to verify the advan-

<sup>1</sup> *Loc. cit.*

tages claimed for it in the detection of methyl alcohol. For our purpose it was found best to employ the reagent very nearly in the manner recommended by Istrati.<sup>1</sup> 0.2 cc. of a saturated solution of gallic acid in pure ethyl alcohol was mixed with a few drops of the oxidized alcoholic solution to be tested, diluted to 2 cc., and the mixture carefully run down the side of an inclined test-tube containing a few cubic centimeters of concentrated sulphuric acid. At the line of contact between the two liquids a yellow zone, almost immediately turning green, makes its appearance, if the solution contains formic aldehyde. Above and below the green zone, blue rings then rapidly develop. If other substances which give color reactions are also present, the upper layer will vary in color, but the green and the lower blue ring will still appear beneath. The colors are pure and characteristic, and are not obscured by the presence of other aldehydes. Having familiarized ourselves with these phenomena, it was with considerable surprise that we found the oxidation-products obtained in the usual way from the purest procurable ethyl, propyl, isopropyl, secondary butyl, tertiary butyl, and normal butyl alcohols, ethylene glycol, glycerin, acetaldehyde, paraldehyde, ethyl ether, acetone, pinacone, and acetic acid, all gave distinct green and blue rings with gallic acid.

The total failure of the gallic acid test to distinguish the substances enumerated from methyl alcohol, as well as the anomalous results noted in our earlier experiments with the oxidation-products from concentrated ethyl alcohol when tested with a trace of resorcine or with caseine, are susceptible of only two simple explanations. Either all the apparently pure compounds oxidized must have contained methyl alcohol or methyl derivatives as impurities, or the list of compounds which may give traces of formic aldehyde upon oxidation with copper oxide is a very much longer one than has hitherto been suspected. The hypothesis that methyl alcohol in small

<sup>1</sup> Analyst, **23**, 230 (abstract) (1898). Istrati's original memoir on the color reactions between aldehydes and phenols (Buletinul Societatei de Stiinte, Bucuresti, vii (2), 163-170) which was made accessible to us through the kindness of M. Jandrier, forms a continuation of the earlier studies of Barbier and Jandrier. Another still earlier research on the value of phenols for the detection of aldehydes, mention of which was also unintentionally omitted in our first paper, is by Nickel (Fres. Zeit. (1889), 249).



quantities may be formed along with ethyl alcohol in alcoholic fermentations is perhaps not unworthy of a more thorough investigation than it has received. Trillat claims to have detected traces of it in some genuine brandies. But it is, nevertheless, highly improbable that all the cases which have been noted by us in which formic aldehyde reactions were obtained from the oxidation-products of the many presumably pure substances taken for our experiments can be explained in this way, and we inclined strongly, from the first, to the acceptance of the second explanation, the probability of which has since become a certainty in consequence of a supplementary quantitative investigation conducted by one of the authors with the assistance of Messrs. Brown and French, an account of which will follow later in this JOURNAL.

The logical justification for adhering to the use of resorcline in the test for methyl alcohol lies, then, in the presumption that no common organic compound that could occur in such solutions as are provided for by the method (with the exception of methyl esters or ethers), will furnish enough formic aldehyde, or other substance, exhibiting a similar behavior, when treated with due regard to the detailed directions to give a rose-red ring and flocks. This presumption is a sufficiently well-founded one, when all the precautions that will be given further on in this paper are observed. The gallic acid and caseine tests, on the contrary, must be rejected, because they are so delicate that formic aldehyde may be detected by their use in nearly any organic solution that has been partially oxidized by means of a copper spiral.

Since the publication of our first paper we have had occasion to apply the resorcline test for methyl alcohol to a great variety of mixtures, and as a consequence of the fuller knowledge of the imperfections of the method thus gained, we are now in a position to suggest certain improvements in the original procedure, which, we believe, will considerably augment its practical usefulness. Analysts are, as a rule, too prone to ignore the fact, that the *absolute* identification of any compound by the use of some single specific reaction is an unattainable end when really unknown mixtures are dealt with. Specific qualitative tests are of great value when judiciously

employed ; but each new mixture must be considered by itself, and whenever there is reason to suspect the presence of substances which may interfere with the test selected, means for their removal must first be devised. The list of compounds whose presence may mask the color reactions given by phenols with formic aldehyde is a long one, and includes bodies which are likely to be met with in such important mixtures as the commercial tinctures, extracts, varnishes, alcoholic beverages, and solvents. While it would be feasible to formulate quite definite rules of procedure for the detection of methyl alcohol in any limited group of mixtures, it will be more profitable here to make certain general suggestions that will be of service in the solution of a variety of special problems.

The following precautions should always be observed :

(a) Use for the test only that part of any mixture that can be completely distilled at a temperature between  $50^{\circ}$  and  $100^{\circ}$ , and which, after distillation, gives a clear colorless solution when shaken with two or three volumes of water.

(b) Make a blank experiment, before oxidation with the copper spiral, by pouring 2 cc. of a clear aqueous solution of the distillate of proper boiling-point, to which 1 drop of 0.5 per cent resorcline solution has been added, so as to form a layer upon concentrated sulphuric acid in a test-tube. If a precipitate or a colored ring make its appearance, the solution requires further preliminary treatment.

(c) Do not test without preliminary treatment any solution that is known or suspected to contain phenols, alkaloids, or organic bases.

The reasons for these precautions are obvious. Many organic compounds give colorations with sulphuric acid alone ; others, including nearly all aldehydes and many bases, condense easily with resorcline under the conditions of the test to insoluble or intensely colored products. Other phenols besides resorcline, and many bases, will, if present, react with any formic aldehyde that may arise by oxidation with the wire, and thus prevent or obscure the appearance of the characteristic rose-red ring.

Methyl alcohol may be separated easily from most coloring-matters, oils, resins, sugars, glycerine, and glycols, by a sim-

ple distillation; from phenols and acids by distillation from an aqueous solution containing caustic alkali; from bases by distillation from aqueous solutions strongly acidified with a dilute mineral acid. When small quantities of methyl alcohol are extracted from insoluble organic mixtures by shaking out with water, it is to be remembered that the methyl alcohol will tend to concentrate in the first part of the aqueous distillates obtained from such solutions, and that various aldehydes, phenols, and bases may pass over with it on account of their volatility with steam, and will have to be removed afterwards.

When the preliminary blank experiment (*b*) gives a coloration or precipitate, and the solution gives aldehydic reactions with ammoniacal silver nitrate and with Schiff's rosaniline-aldehyde reagent, take 12 cc. of the alcoholic distillate, which, if concentrated, must first have been diluted so as to contain at least 75 per cent of water; place in a small firmly stoppered bottle with 3 grams of resorcine and 1 cc. strong sulphuric acid, and heat for two hours in a water-bath at 70°–80°. Cool, dilute the solution to 50 cc. with water, distil off 5 cc., and test the distillate for methyl alcohol in the usual manner. Large quantities of aldehydes may be held back by resorcine in this way, though, when the mixture consists mainly of aldehydes, more resorcine and longer heating will be required. An analogous method for accomplishing this same result, which employs aniline and phosphoric acid instead of resorcine and sulphuric acid, was proposed by Allen and Chattaway<sup>1</sup> for use in the analysis of whiskies. We have used both these methods with success upon mixtures containing as high as 50 per cent of furfural and other aldehydes, thus meeting the chief objection which Jandrier has raised against our procedure.

A more difficult, but practically far more important, problem than that of removing aldehydes from the original mixtures, had to be faced, when we sought to discover some simple means for taking away the acetaldehyde which is always formed together with formic aldehyde when mixtures containing both ethyl and methyl alcohols are oxidized. The

<sup>1</sup> Analyst, 16, 102.

most that could be previously claimed for the test with resorcin in such mixtures was, that "One part of methyl alcohol may be detected without great difficulty in the presence of five parts of ethyl alcohol." A simple and fairly satisfactory way out of this difficulty was, however, found.

Acetaldehyde is easily and completely expelled from aqueous solutions by persistent boiling in a vessel provided with some condensing arrangement that will prevent too rapid loss of water vapor. Dilute solutions of formic aldehyde, on the contrary, lose their aldehyde very slowly under this treatment, it being firmly held, partly in a polymerized condition, by the hot water. Such solutions will, however, lose all their formic aldehyde when the distillation is rapid and is pushed too far. The improved test for methyl alcohol now to be described takes advantage of these facts, and as the procedure not only removes acetaldehyde, but also traces of many other higher boiling substances that exert an injurious influence on the final color reaction, its employment is generally to be preferred to the somewhat simpler method earlier described by us.

When entirely unknown mixtures are under examination they must, of course, always receive in addition a suitable preliminary treatment, though it has been found that a previous digestion with resorcin and acid for the removal of aldehydes, will seldom be required when these substances are not present in larger quantities than are usually found in the distillates from fermented and distilled liquors.

Unless the mixture to be examined, after receiving whatever preliminary treatment may have been found necessary, already contains much water, dilute 2 cc. with water until it measures 6 cc. Treat with the oxidized copper spiral as elsewhere described, six times, cooling the tube with running water after each treatment. Next fit the test-tube, which should have a length of 6-7 inches, with a doubly perforated rubber stopper. One perforation of the stopper is to be fitted with a piece of glass tubing drawn out to a *very fine capillary* whose end is forced down so as nearly to touch the bottom of the tube. Let the wide end of the tube, on which the capillary has been drawn, project an inch above the stopper, and attach to the projecting end a bit of rubber connector which

can be closed by a small screw clamp. Fit the second perforation of the stopper with a bit of glass tubing which is placed in connection with a good water suction-pump capable of giving a vacuum of about 20 mm. Support the test-tube by a clamp, so that it will be two-thirds immersed in water in a beaker maintained at 25°-30°. Partially close the screw clamp and apply gentle suction for a few moments so as thoroughly to saturate the liquid with air. Then screw the clamp tight and apply suction with the full power of the pump. A rapid stream of gas bubbles, at first principally air, but later consisting of acetaldehyde, alcohol, and water vapor, will rise from the fine capillary point, the liquid boiling under the diminished pressure. Continue this distillation *in vacuo* until just one-half of the liquid has evaporated. This requires about ten minutes. By judiciously regulating the action of the pump, and in some cases admitting a very little air through the capillary, the boiling, though accompanied by some frothing, is easily controlled, and bumping prevented.<sup>1</sup> Next add 1 drop of a solution, containing 1 part of resorcline in 200 parts of water to the residual solution, and pour it cautiously into a second tube held in an inclined position in such a way that the two liquids shall not mix. Allow it to stand three minutes; then, holding the tube by its upper end, sway it slowly from side to side in such a manner as to produce a very gentle rotary motion between the two layers. This operation must be persisted in if necessary, for a minute or more, using a piece of white paper for a background; but must be conducted so gently that only a very gradual and partial mixing of the water and acid shall be caused. Nearly half of the acid should remain as a distinct unmixed layer at the end. When methyl alcohol is present, the shaking causes the separation of more or less voluminous flocks of a very characteristic rose-red color. The appearance of colored zones or flocks of other hues, even when tinged with red, or of a rose-red solution without the flocks, should never be considered proof of the presence of methyl alcohol. However, if the flocks are red-

<sup>1</sup> An experienced operator may often obtain equally satisfactory results by simply boiling down the oxidized aqueous solution in an open test-tube until the moment when the odor of acetaldehyde disappears. The method of boiling down *in vacuo* is, however, in general, much more reliable.

dish-brown, or if the upper layer has a pronounced red color, it is often well to repeat the test. Too hasty or careless mixing of the aqueous and acid layers spoils the reaction, which will also fail or give unsatisfactory results if the evaporation *in vacuo* is too long continued, or if it is stopped before the complete removal of all acetaldehyde.

The delicacy of the test as here described is sufficient to permit the detection of 1 part of methyl alcohol in 2000 parts of the solution as prepared for oxidation. If, in a solution of moderate concentration, the proportion of ethyl to methyl alcohol does not exceed 100 parts to 3, entirely satisfactory tests for the latter are obtained without difficulty. When the ratio between the alcohols is 100 : 2, the test is occasionally successful, but cannot be depended upon.

Besides methyl alcohol, the only substances which are known to give the same reaction with the improved resorcline test are the methyl esters and ethers (including methylal), and secondary and butyl alcohols (compounds which are rarely met with except in quantities too small to be readily detected). Acetone and dimethylethyl carbinol give red rings at first, but on shaking, the aqueous layer becomes red-brown without yielding the rose-colored flocks.

As compared with other qualitative tests for methyl alcohol known at the time of writing, the one just presented is without question the simplest, the most rapid, and the most convenient. Its delicacy, while not great, is sufficient for most practical purposes, and its most serious imperfections are so well defined as to be rendered comparatively harmless.

CHEMICAL LABORATORY,  
MASS. INST. OF TECHNOLOGY,  
August, 1900.

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## ON SOME DERIVATIVES OF $\alpha$ -NITRO- $\beta$ -DINITRO- PROPIONIC ALDEHYDE.

BY JOSEPH TORREY, JR., AND OTIS FISHER BLACK.

We have been engaged in a study of the orange-red potassium salt obtained by Hill and Sanger<sup>1</sup> as the principal product of the reaction between mucobromic acid and potassic

<sup>1</sup> Ber. d. chem. Ges., **15**, 1906 (1882).

nitrite in dilute alcoholic solution, and shown by the same investigators to have the formula  $K_2C_3HN_3O_7$ .

The investigation has been a difficult one from the start, but the experimental results reached thus far seem to show conclusively that the substance under study is the dipotassium salt of  $\alpha$ -nitro- $\beta$ -dinitropropionic aldehyde; a view which was first suggested by the ease with which the salt passes into what is now known to be potassium nitromalonic aldehyde<sup>1</sup> on heating with water or with dilute alcohol.

In following out this idea it was obviously necessary to establish the presence of an aldehyde group in the molecule, but our first experiments, which were naturally directed to the ordinary aldehyde reactions, were not very satisfactory. Hydroxylamine, though tried under every condition we could devise, yielded us no oxime capable of being isolated; free phenylhydrazine yielded the dihydrazone of nitromalonic aldehyde, while phenylhydrazine hydrochlorate yielded 1-phenyl-4-nitropyrazole. Both these latter bodies have been described by H. B. Hill and one of us,<sup>2</sup> and their appearance here has significance as emphasizing the relationship between the body under study and nitromalonic aldehyde derivatives. With aniline we have had better success. The first results we reached were of the same nature as those just noted in case of phenylhydrazine; *i. e.* we obtained the anil of nitromalonic aldehyde, but we soon found that under different conditions the reaction took a totally different turn, and a careful study of the products obtained in the different reactions has led to results which appear to be decisive.

Free aniline has no action upon the potassium salt, either in neutral or alkaline solution; but the aniline salts react readily, and the nature of the reaction is determined by the presence or absence of free strong acid in the solution. In presence of free hydrochloric acid, for example, nitromalonic aldehyde anil is always obtained, but when there is no free strong acid in the solution the reaction takes another course. When the aqueous solution of the potassium salt is mixed with aniline acetate, or with aniline hydrochlorate in presence

<sup>1</sup> This JOURNAL, 22, 89 (1899).

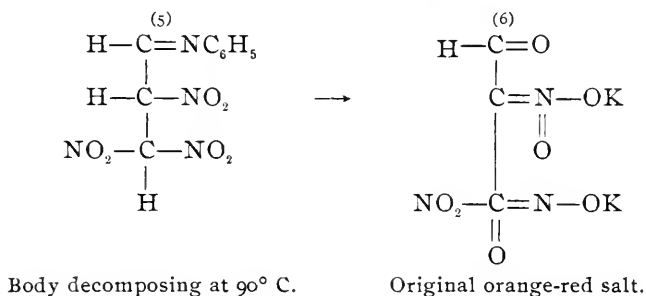
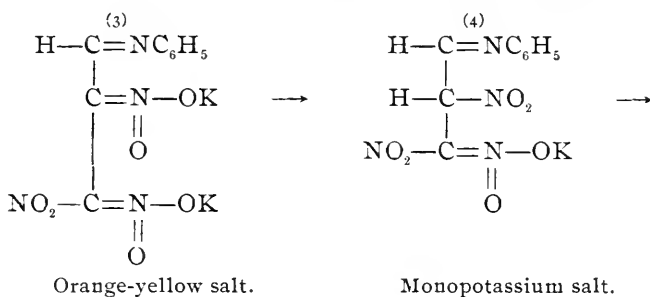
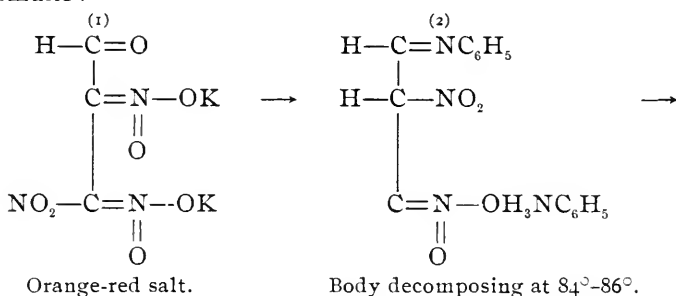
<sup>2</sup> *Loc. cit.*

of sodic acetate, a deep yellow substance is precipitated, and this substance, when washed with ether becomes bright lemon-yellow, the ether having washed out a small quantity of a dark-brown oil, which is produced by a side reaction and which causes the slightly darker color of the substance as first precipitated. This bright-yellow substance decomposes at  $84^{\circ}$ - $86^{\circ}$  and proves, on analysis, to have the formula  $C_{15}H_{15}N_5O_6$ . Aqueous potash dissolves it, and on adding alcohol there separates an orange-yellow potassium salt whose formula is  $K_2C_9H_6N_4O_6$ . Evidently the action of potash upon the yellow substance consists in the elimination of a molecule of aniline, and the replacement of two hydrogen atoms by potassium. On acidifying the aqueous solution of the new potassium salt with any strong acid, there separates a second lemon-yellow substance decomposing at  $90^{\circ}$  and having the formula  $C_9H_5N_4O_6$ . The reaction is a perfectly clean one, and consists simply in the replacement of potassium by hydrogen. Finally, on heating the lemon-yellow body with alcoholic potash, there crystallizes out from the cooled solution the original orange-red potassium salt,  $K_2C_3HN_3O_7$ . In this reaction, then, the phenylimido group has been removed, and its place taken by oxygen, which makes it highly probable that the lemon-yellow substance decomposing at  $90^{\circ}$  is the anil of the substance  $C_3H_3N_3O_7$ , which is the free body corresponding to the orange-red potassium salt. Moreover, it will be noticed that the formula of the orange-red salt ( $K_2C_3HN_3O_7$ ) differs from that of the orange-yellow salt ( $K_2C_9H_6N_4O_6$ ) in that in the latter oxygen has been replaced by the phenylimido group; here again the relation is that existing between an aldehyde or a ketone and its anil.

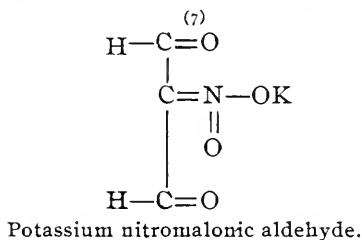
The ready transition to derivatives of nitromalonic aldehyde, together with the formation of an anil, point decidedly to the presence of an aldehyde group in the molecule of the orange-red potassium salt, and also to the presence of a nitro group on the carbon atom adjoining the aldehyde carbon. Furthermore, when the orange-yellow salt is treated, in aqueous solution, with acetic, or even carbonic acid, one atom of potassium is split off, and a monopotassium salt is obtained, a fact which suggests different environment of the two acid hydrogens.



All these facts find a ready explanation in the following formulæ :



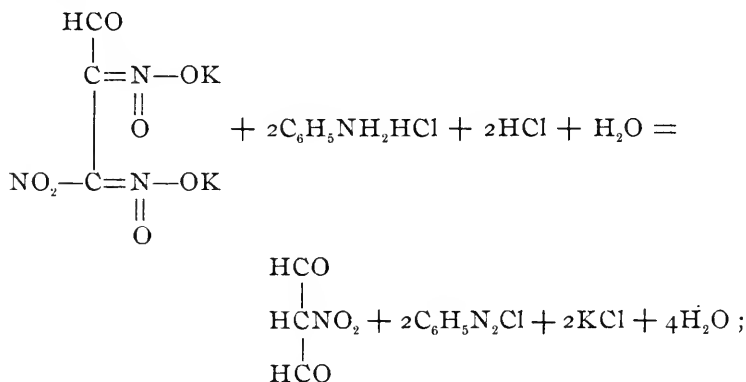
which, heated with water or alcohol, gives :



According to this view, the orange-red salt is the dipotassium salt of  $\alpha$ -nitro- $\beta$ -dinitropropionic aldehyde.<sup>1</sup> The body obtained by the action of aniline acetate is an aniline salt of  $\alpha$ -nitro- $\beta$ -dinitropropionic aldehyde anil. The orange-yellow salt is the dipotassium salt of  $\alpha$ -nitro- $\beta$ -dinitropropionic aldehyde anil. This, when treated with acid, gives the free anil, which finally yields, on treatment with alcoholic potash, the original orange-red potassium salt of the aldehyde.

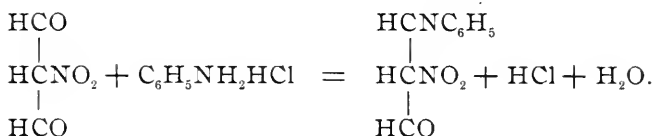
These formulæ received unexpected and substantial confirmation when the reaction between the orange-red salt and aniline in presence of strong acids came to be studied more carefully. With 3 molecules of aniline and excess of hydrochloric acid there is a quantitative precipitation of nitromalonic aldehyde anil, and the filtrate contains diazobenzol chloride. By drying and weighing the precipitated anil, and by precipitating the diazobenzol by means of an alkaline solution of  $\beta$ -naphthol, as the nearly insoluble benzol-azo- $\beta$ -naphthol, we found that for every molecule of the potassium salt present we obtained 1 molecule of nitromalonic aldehyde anil and 2 molecules of diazobenzol.<sup>2</sup>

The elimination of two nitro groups from each molecule of the potassium salt, and the formation of the theoretical quantity of nitromalonic aldehyde anil can only be explained as follows :



<sup>1</sup> Throughout the remainder of this paper the parent substance of the derivatives there described will be called trinitropropionic aldehyde. There is no present danger of any confusion arising.

<sup>2</sup> The yield was, in each case, 91 per cent of the theoretical.



Paratoluidine forms derivatives analogous in constitution to those yielded by aniline, and of much the same appearance. Methylamine reacts similarly so far as our studies have extended. These derivatives are described in the sequel.

We have made some attempts to obtain from the potassium salt the free trinitropropionic aldehyde. When the carefully dried potassium salt is brought into a solution of hydrogen chloride in absolute ether, potassic chloride separates and the ether extract yields, on evaporation, a colorless oil having an odor something like that of nitroethane. This oil, on standing for a few minutes at the ordinary temperature, undergoes a sudden and tumultuous decomposition. If treated with alcoholic potash as soon as the ether has evaporated, it yields the original orange-red salt, so it is undoubtedly the free aldehyde, but, owing to its marked instability, we have thus far made no more experiments upon it.

*Di-potassium Salt of α-Nitro-β-dinitropropionic Aldehyde (Dipotassium Trinitropropionic Aldehyde), K<sub>2</sub>C<sub>3</sub>HN<sub>3</sub>O<sub>7</sub>.*—This body was first described and analyzed by Hill and Sanger in 1882. It is best prepared as follows: Mucobromic acid (20 grams) is dissolved in 70 cc. alcohol, and a saturated aqueous solution of potassic nitrite (26 grams) added. The solution separates into two layers on standing for a minute or two, and water is added in small quantities, with shaking, until the whole becomes homogeneous. In a few moments the action sets in, with effervescence and rise in temperature. The best results are obtained by keeping the mixture at 30°–35°, and the action is over in about half an hour. Considerable of the potassium salt separates in fine orange-red crystals during the last fifteen minutes, and on cooling a further quantity is obtained. The ordinary yield is about 15 grams. The salt is easily purified by solution in water and precipitation with alcohol. As thus prepared, it is very stable under ordinary conditions, and specimens have been kept exposed to the air

for a year without showing any sign of decomposition. It is also stable in slightly alkaline solution, but decomposes in acid solution.

The analyses here given are taken from Hill and Sanger's paper.<sup>1</sup>

	Calculated for $K_2C_8H_7N_5O_7$ .	I.	Found. II.	III.	IV.
C	13.38	13.46	13.68	....	....
H	0.37	0.69	0.68	....	....
N	15.59	15.42	15.81	15.02	....
K	29.05	28.94	28.61	28.80	28.80

*Aniline Salt of Trinitropropionic Aldehyde Anil*,  $C_{15}H_{15}N_5O_6$ .—When a water solution of the orange-red salt<sup>2</sup> is mixed with a solution of aniline acetate, or with a solution of aniline hydrochlorate containing excess of sodic acetate, the aniline salt of the anil is precipitated. The best results are obtained when 2 molecules of aniline acetate or hydrochlorate are present for every molecule of the orange-red salt. A very slight excess of acid gives rise to side reactions, the principal product of which is a brownish oil which has not been further studied. The yellow precipitate is well washed with ether, by which means it is obtained pure enough for analysis. We have been unable to find any practicable way of purifying it by crystallization:

I. 0.2178 gram substance gave 0.3925 gram  $CO_2$ , and 0.0849 gram  $H_2O$ .

II. 0.2117 gram substance gave 0.3855 gram  $CO_2$ , and 0.0804 gram  $H_2O$ .

III. 0.1795 gram substance gave 30.7 cc. moist nitrogen at  $20^\circ$  and under a pressure of 760.5 mm.

	Calculated for $C_{15}H_{15}N_5O_6$ .	I.	Found. II.	III.
C	49.82	49.14	49.67	....
H	4.18	4.33	4.22	....
N	19.44	....	....	19.69

The freshly prepared substance consists of minute lemon-yellow crystals which darken slightly on exposure, though the composition does not seem to alter materially. With acids it

<sup>1</sup> Ber. d. chem. Ges., **15**, 1907.

<sup>2</sup> This method of designating dipotassium trinitropropionic aldehyde will be followed throughout the present paper.

undergoes an apparently complicated decomposition, one of the products being a diazobenzol salt. The action of alkalies will be described farther on. The crystals are soluble in acetone and somewhat in alcohol, but are nearly insoluble in water and in ether. In the melting-tube they decompose with a puff at  $84^{\circ}$ - $86^{\circ}$ .

*Dipotassium Trinitropropionic Aldehyde Anil*,  $K_2C_9H_6N_4O_6 \cdot 3H_2O$ .—When the aniline salt just described is dissolved in cold potassic hydroxide, alcohol precipitates from the solution a red, crystalline substance, which, when dried in the air, takes on a permanent orange-yellow color. The same substance is obtained when trinitropropionic aldehyde anil, soon to be described, is dissolved in alcoholic potash, or, still better, is dissolved in acetone, and the solution precipitated by alcoholic potash. Analysis shows that the substance thus obtained has the formula given above. The material analyzed was purified by solution in water and precipitation with alcohol. The air-dried salt carries 3 molecules of crystal water. One of them is readily given up over concentrated sulphuric acid. The others cannot be determined directly as the temperature at which the water is given off is above the decomposition point of the salt.

I. 0.2702 gram air-dried salt lost 0.0137 gram over  $H_2SO_4$ .

II. 0.2565 gram substance dried over  $H_2SO_4$  gave 0.1162 gram  $K_2SO_4$ .

III. 0.1880 gram substance dried over  $H_2SO_4$  gave 0.0871 gram  $K_2SO_4$ .

	Calculated for $K_2C_9H_6N_4O_6 \cdot 3H_2O$ .		Found.
1 mol $H_2O$	4.52		5.07
	Calculated for $K_2C_9H_6N_4O_6 \cdot 2H_2O$ .	I.	Found. II.
K	20.56	20.80	20.34

When the anil is used in preparing this salt the yield is quantitative. When the aniline salt is used, the alcoholic filtrate from the potassium salt contains nitromalonic aldehyde dianil, which slowly crystallizes out on standing, in long, silky, yellow needles.

*Trinitropropionic Aldehyde Anil*,  $C_9H_8N_4O_6$ .—This substance may be obtained either from its aniline salt or from its potas-

sium salt. When the aniline salt is dissolved in potassic hydroxide and the solution acidified with hydrochloric acid, the anil is precipitated together with some nitromalonic aldehyde anil. A purer product is obtained by dissolving the aniline salt in potassic carbonate, constantly shaking the mixture with a layer of ether, which extracts the liberated aniline. The aqueous solution is then filtered and acidified with hydrochloric acid. The first stage of the reaction consists in the elimination of aniline and formation of the potassium salt of the anil, which, when acidified, gives the free anil. This substance is light-yellow in color and decomposes at  $90^{\circ}$ . It is soluble in acetone but insoluble in most other common solvents. Heated with alcoholic potash it gives a large yield of dipotassium trinitropropionic aldehyde.

The material used in the following analysis was purified by dissolving it in acetone and adding ligroin, when the anil slowly separates in light-yellow needles :

I. 0.2049 gram substance gave 0.3051 gram  $\text{CO}_2$ , and 0.0613 gram  $\text{H}_2\text{O}$ .

II. 0.2111 gram substance gave 0.3116 gram  $\text{CO}_2$ , and 0.0616 gram  $\text{H}_2\text{O}$ .

III. 0.1623 gram substance gave 30 cc. moist nitrogen at  $23^{\circ}.5$  and under a pressure of 761 mm.

	Calculated for $\text{C}_9\text{H}_5\text{N}_4\text{O}_6$ .	I.	Found. II.	III.
C	40.26	40.61	40.26	....
H	3.00	3.25	3.24	....
N	20.94	....	....	20.94

*Monopotassium Trinitropropionic Aldehyde Anil*,  $\text{KC}_9\text{H}_7\text{N}_4\text{O}_6$ .

—When the dipotassium salt of the anil is dissolved in the smallest possible amount of water, and acidified with a weak acid (acetic acid was generally used) a monopotassium salt of the above formula separates in light-yellow crystals.

0.1980 gram substance gave 0.0568 gram  $\text{K}_2\text{SO}_4$ .

	Calculated for $\text{KC}_9\text{H}_7\text{N}_4\text{O}_6$ .	Found.
K	12.77	12.87

It is much less soluble in water than the normal salt. Treated with hydrochloric acid it gives the free anil ; with alcoholic potash the normal salt is obtained.

*Barium Trinitropropionic Aldehyde Anil*,  $\text{BaC}_9\text{H}_6\text{N}_4\text{O}_6 \cdot 5\text{H}_2\text{O}$ .—This salt is obtained by mixing aqueous solutions of the dipotassium salt of the anil and baric chloride, or by dissolving the free anil in baric hydroxide. It is sparingly soluble in cold water, more so in warm water, and insoluble in alcohol. It may be purified by dissolving it in water at  $35^\circ$ , then cooling and adding alcohol when the pure salt separates in small, red, gleaming plates.

As thus prepared, purified, and air-dried the salt contains 5 molecules of crystal water, of which three are given up over sulphuric acid.

I. 0.2522 gram salt (air-dried) lost 0.0286 gram over  $\text{H}_2\text{SO}_4$ .

II. 0.2236 gram salt, dried over  $\text{H}_2\text{SO}_4$ , gave 0.1173 gram  $\text{BaSO}_4$ .

III. 0.1749 gram salt, dried over  $\text{H}_2\text{SO}_4$ , gave 0.0917 gram  $\text{BaSO}_4$ .

	Calculated for $\text{BaC}_9\text{H}_6\text{N}_4\text{O}_6 \cdot 5\text{H}_2\text{O}$ .		Found.
$3\text{H}_2\text{O}$	10.92		11.34
	Calculated for $\text{BaC}_9\text{H}_6\text{N}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ .	II.	Found.
Ba	31.18	30.87	III. 30.87

*p-Toluidine Salt of Trinitropropionic Aldehyde p-Tolil*,  $\text{C}_{17}\text{H}_{19}\text{N}_5\text{O}_6$ .—This substance is very similar in appearance and in properties to the corresponding aniline compound. It can be prepared by adding *p*-toluidine hydrochlorate to an aqueous solution of the orange-red salt, or better, by adding *p*-toluidine hydrochlorate and acetic acid to the dipotassium salt of the *p*-tolil in aqueous solution. As all attempts to recrystallize it resulted unfavorably, it was prepared for analysis by the second of the two methods above mentioned, using as pure material as possible:

0.1977 gram substance gave 0.0896 gram  $\text{H}_2\text{O}$  and 0.3769 gram  $\text{CO}_2$ .

	Calculated for $\text{C}_{17}\text{H}_{19}\text{N}_5\text{O}_6$ .	Found.
C	52.38	51.98
H	4.92	5.07

*Trinitropropionic Aldehyde p-Tolil*,  $\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_6$ .—By dissolving the *p*-toluidine salt just described in potassic carbonate

and acidifying with hydrochloric acid, the tolil is obtained; but the process is much slower since the separated *p*-toluidine coats the undissolved crystals. By shaking with a layer of ether this difficulty may be partly overcome. The tolil is very similar to the anil and is purified in a similar manner.

I. 0.1903 gram substance gave 0.2954 gram  $\text{CO}_2$ , and 0.0625 gram  $\text{H}_2\text{O}$ .

II. 0.1664 gram substance gave 29.8 cc. moist nitrogen at  $26^\circ$  and under a pressure of 751.5 mm.

	Calculated for $\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_6$ .	Found
C	42.51	42.33
H	3.57	3.67
N	19.90	19.54

*Dipotassium Trinitropropionic Aldehyde-p Tolil*,  $\text{K}_2\text{C}_{10}\text{H}_8\text{N}_4\text{O}_6 \cdot \text{H}_2\text{O}$ .—This salt is perfectly analogous to the corresponding salt of the anil. It is prepared by adding alcoholic potash to an acetone solution of the *p*-tolil. It is orange-red in color and contains a molecule of crystal water after drying over sulphuric acid.

I. 0.2001 gram salt gave 0.0911 gram  $\text{K}_2\text{SO}_4$ .

II. 0.2473 gram salt gave 0.1127 gram  $\text{K}_2\text{SO}_4$ .

	Calculated for $\text{K}_2\text{C}_{10}\text{H}_8\text{N}_4\text{O}_6 \cdot \text{H}_2\text{O}$ .	I.	Found.	II.
K	20.79	20.44		20.41

*Monopotassium Trinitropropionic Aldehyde p-Tolil*,  $\text{KC}_{10}\text{H}_8\text{N}_4\text{O}_6$ .—The acid properties of the tolil are somewhat weaker than those of the anil. When acetic acid is added to an aqueous solution of the dipotassium salt, the mixture of the monopotassium salt with some free tolil is precipitated. Carbonic dioxide, however, works satisfactorily, and the pure mono salt is obtained. It is yellow in color and is anhydrous.

0.2382 gram salt gave 0.0646 gram  $\text{K}_2\text{SO}_4$ .

	Calculated for $\text{KC}_{10}\text{H}_8\text{N}_4\text{O}_6$ .	Found.
K	12.22	12.17

*Barium Trinitropropionic Aldehyde p-Tolil*,  $\text{BaC}_{10}\text{H}_8\text{N}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ .—The *p*-tolil dissolves in baric hydroxide, forming a red solution from which separates a red salt very similar to the barium salt of the anil. The air-dried salt carries 4 mole-



cules of crystal water, of which it gives up three when dried over sulphuric acid.

I. 0.2229 gram air-dried salt lost 0.0250 gram over  $\text{H}_2\text{SO}_4$ .

II. 0.2600 gram air-dried salt lost 0.0279 gram over  $\text{H}_2\text{SO}_4$ .

III. 0.1979 gram salt dried over  $\text{H}_2\text{SO}_4$  gave 0.1049 gram  $\text{BaSO}_4$ .

IV. 0.2321 gram salt dried over  $\text{H}_2\text{SO}_4$  gave 0.1237 gram  $\text{BaSO}_4$ .

	Calculated for $\text{BaC}_{10}\text{H}_8\text{N}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ .	I.	Found.	II.
$3\text{H}_2\text{O}$	11.04	11.21		10.73
	Calculated for $\text{BaC}_{10}\text{H}_8\text{N}_4\text{O}_6 \cdot \text{H}_2\text{O}$ .	III.	Found.	IV.
Ba	31.54	31.19		31.36

#### *Action of Methylamine.*

When methylamine hydrochlorate is added to an aqueous solution of the orange-red salt, the hydrochlorate seems to cause decomposition of the potassium salt as a weak acid would do. If, however, the two are mixed in alkaline solution, the monopotassium salt of trinitropropionic aldehyde methylimide is precipitated. We have also obtained the dipotassium salt and the free methyl imide.

*Monopotassium Trinitropropionic Aldehyde Methylimide*,  $\text{KC}_4\text{H}_5\text{N}_4\text{O}_6$ .—In the preparation of this salt we obtained the best results by suspending the finely powdered orange-red salt in a little ammonia and adding rather more than the calculated quantity of methylamine hydrochlorate. The salt begins to separate after the solution has stood for a few minutes. It is light-yellow, explodes when heated, and is sparingly soluble in water and in alcohol. Specimens have been kept exposed to the air for two years without any perceptible change. For analysis it was crystallized from carefully warmed dilute alcohol.

I. 0.1490 gram salt gave 0.0524 gram  $\text{K}_2\text{SO}_4$ .

II. 0.1440 gram salt gave 0.0506 gram  $\text{K}_2\text{SO}_4$ .

	Calculated for $\text{KC}_4\text{H}_5\text{N}_4\text{O}_6$ .	I.	Found.	II.
K	16.02	15.79		15.78

*Dipotassium Dinitropropionic Aldehyde Methylamide*,  $\text{K}_2\text{C}_4\text{H}_4$ .

$\text{N}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$ .—When the monopotassium salt is dissolved in potassic hydroxide, alcohol precipitates a bright-yellow, highly crystalline salt. Its analysis showed that it was analogous to the dipotassium salts already mentioned.

I. 0.1948 gram substance (air-dried) gave 0.1000 gram  $\text{K}_2\text{SO}_4$ .

II. 0.1658 gram air-dried salt gave 0.0852 gram  $\text{CO}_2$ , and 0.0511 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{K}_2\text{C}_4\text{H}_4\text{N}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$ .	Found.
K	23.26	23.04
C	14.27	14.00
H	2.99	3.44

*Trinitropropionic Aldehyde Methylimide*,  $\text{C}_4\text{H}_6\text{N}_4\text{O}_6$ .—The monopotassium salt above described is the most convenient starting-point in preparing the free imide. A saturated solution of the salt in water is acidified with hydrochloric acid, when the imide separates in snow-white, pearly crystals. It is sparingly soluble in water, very soluble in acetone, and insoluble in ether. It is best purified by solution in acetone and precipitation by ether.

I. 0.1948 gram substance gave 0.1668 gram  $\text{CO}_2$ , and 0.0513 gram  $\text{H}_2\text{O}$ .

II. 0.1794 gram substance gave 42.6 cc. moist nitrogen at  $18^\circ$  and under a pressure of 755 mm.

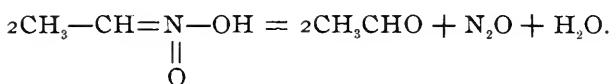
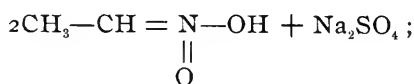
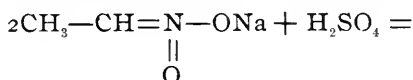
	Calculated for $\text{C}_4\text{H}_6\text{N}_4\text{O}_6$ .	I.	Found.	II.
C	23.27	23.35		....
H	2.93	2.94		....
N	27.24	....		27.14

In this paper, as well as in the previous publications of Hill and Torrey on nitromalonic aldehyde, there are recorded a number of cases where the alkali salts of paraffin nitro bodies have yielded the free body on acidification; in fact this has been the rule, to which we have thus far encountered no exception, though the free body has sometimes proved unstable or has undergone condensation on standing. These results are interesting in connection with Nef's work on the constitution of the nitroparaffins. For instance, he has shown<sup>1</sup> that

<sup>1</sup> Ann. Chem. (Liebig), 280, 264 et seq.

when the sodium salts of the primary nitroparaffins are acidified, aldehydes are obtained, ketones being produced in case of secondary nitro bodies.

With sodium nitroethane, 69.7 per cent of the theoretical quantity of acetaldehyde was obtained. Sodium nitromethane yields a very small amount of free nitromethane together with formic aldehyde. According to Nef, the free body passes at once into the aldehyde by intramolecular oxidation, thus :



These facts have played a somewhat important part in the development of Nef's views on the constitution of the alkali salts of the nitroparaffins.

It will be noticed that most of the bodies described in this paper, and in the others to which we have referred, are secondary nitro bodies, and that the only ones carrying a nitro group on a terminal carbon, are trinitropropionic aldehyde, with its anil, *p*-tolil, and methylimide. Furthermore, they are all derivatives of nitroparaffin aldehydes and their condensation-products. Most of them are solids, insoluble or sparingly soluble in water, trinitropropionic aldehyde alone being a liquid. Taken as a whole, they constitute a group of paraffin-nitro bodies of remarkable stability.

As was previously stated, considerable difficulty has been encountered in the details of the investigation ; the analytical work, in particular, being often troublesome. It is with pleasure that we acknowledge many valuable and timely suggestions, particularly from Professor H. B. Hill.

## OBITUARY.

SIR JOHN BENNET LAWES.

The originator of many of the methods now used in the scientific study of agricultural processes, and the founder of the first experiment station, after which the State Agricultural Experiment Stations were modeled, died recently at the age of eighty-six. Sir John Lawes was educated at Eton and Oxford and showed his interest in chemistry, after leaving college, by fitting up a laboratory in a barn on his estate at Rothamsted, Herts, where he manufactured calomel, on a commercial scale, by a method which had been recently introduced. In 1837 he began to study the action of various substances on growing plants and to compare the relative values of different fertilizing substances. He carried on experiments with ground bone, both fresh and burned, and phosphatic rocks, and was especially impressed with the great increase in the value of the material, as a manure, after it had been partly converted into more soluble compounds by treatment with sulphuric acid. In 1842 he patented the process for treating apatite and other phosphatic minerals with sulphuric acid to produce the superphosphates, a process which has rendered available a large and comparatively cheap supply of the phosphorus necessary for plant growth. His commercial energy led him to establish a number of factories for the manufacture of manures, and later for the preparation of tartaric and citric acids.

He was able to carry on experiments on many problems relating to agricultural science, at the same time that his attention was given to directing his commercial undertakings, through the assistance of Dr. J. H. Gilbert, whose name has been associated with all the work since 1843. The ground devoted to the experimental work, consisting of 40 acres, was divided into small lots upon which the crops were raised in the usual rotation. A careful record of each lot was kept and the reports upon all kinds of problems, which suggested themselves for experimentation, fill more than nine volumes. The value of his work was quickly recognized by the agriculturists of England, who expressed their appreciation of his efforts by building and presenting to him a laboratory to replace the barn, which had long since been outgrown. In order that the work might suffer no interruption at his death, he transferred the experimental grounds and a fund of £100,000 to a board of trustees. His great influence in extending and ad-

vancing the agricultural pursuits and his valuable contributions to science earned for him many honors from societies in his own country and abroad, and in 1882 he was created a baronet. He also directed his attention to raising the condition of the agricultural worker by the example he set in his method of treatment of his people at Rothamsted, where libraries and schools and other sources of improvement were established.

J. E. G.

### NOTE.

#### *On the Zinc-Copper Couple for Preparing Zinc Ethyl.*

Lachman, some time ago, published a method for the preparation of a zinc-copper couple from zinc dust, and has recently given<sup>1</sup> as a reason for the use of his method the difficulty of preparing zinc filings. It may be worth while to call attention to the fact that a very satisfactory and efficient couple may be prepared from Baker & Adamson's zinc, powdered to pass a 30-mesh sieve, and Kahlbaum's reduced copper. Mix 9 parts of the zinc with 1 part of the copper in a small, round-bottomed flask, and close the latter with a cork bearing a small glass tube. Heat gently over a free flame, turning all the time, till the mass becomes gray and loses its luster, but not till there is any sign of fusion. Seal the glass tube and allow to cool. See "Organic Chemistry for the Laboratory," p. 228.

W. A. NOYES.

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### REVIEWS.

JAHRBUCH DER CHEMIE. Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie. Unter Mitwirkung von H. Beckurts (Braunschweig), C. A. Bischoff (Riga), E. F. Dürre (Aachen), J. M. Eder (Wien), P. Friedlaender (Wien), C. Haeussermann (Stuttgart), F. W. Küster (Clansthal), J. Lewkowitsch (London), M. Märcker (Halle), W. Muthmann (München), F. Röhmman (Breslau), herausgegeben von RICHARD MEYER (Braunschweig). IX Jahrgang. 1899. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1900.

It is always a pleasure to welcome a new volume of this valuable publication. It has become indispensable to chemists. Not only can they find in it references to the important articles of the year but they find also interesting introductions to some sections, so that it may be profitably read. Those who do not regularly receive it are advised to subscribe for it at once.

I. R.

<sup>1</sup> This JOURNAL, 24, 31.

EXPERIMENTAL CHEMISTRY. By LYMAN C. NEWELL, PH.D., Instructor in Chemistry at the State Normal School, Lowell, Mass. Boston: D. C. Heath & Co. 1900. 410 pp.

This is a clearly written book and one that is for the most part free of those faults that one commonly meets with in elementary books on chemistry. The author is evidently a good teacher. He thinks logically and expresses himself clearly. Much weight is given to the experimental side of the subject, and quantitative experiments are more numerous than in most similar books. Whether, under the conditions that prevail in our schools, it is possible for the pupils to perform more than a comparatively small part of these experiments is a question that naturally suggests itself. But, of course, the same question suggests itself in connection with every other book of the kind.

I. R.

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*Addition to the Article by George A. König, page 373.*

For the generation of hydrogen sulphide I find that 5 per cent sulphuric hydrate is best adapted. If this dilute acid drops at the rate of 6 cc. a minute, a strong current of the gas will be produced. Repeated titrations have shown that an efficiency of 90 per cent can be obtained. The outflow of the spent acid liquid should be in a level with the copper screen at the bottom of the generating tube.

In generating hydrogen gas I use acid of the same strength but I add sufficient platinum tetrachloride to impart a distinct straw-yellow color.

For carbon dioxide I use a 5 per cent solution of hydrogen chloride.

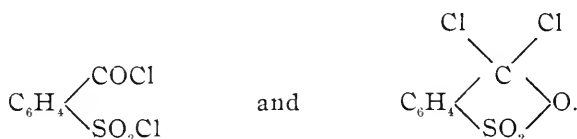
# AMERICAN CHEMICAL JOURNAL

## ON PARANITROORTHOTOLYLPHENYLSULPHONE AND SOME OF ITS DERIVATIVES.<sup>1</sup>

BY R. S. NORRIS.

### INTRODUCTION.

In a series of investigations carried on in this laboratory on derivatives of orthosulphobenzoic acid, it has been shown that when its potassium salt is treated with phosphorus pentachloride two isomeric chlorides are formed,<sup>2</sup> the formulas of which appear to be :



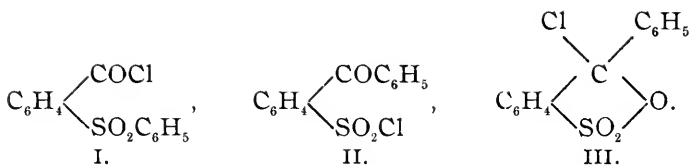
On treating either of these chlorides with aluminium chloride and benzene, one of the chlorine atoms is replaced by a phenyl group; and the products formed are in both cases identical.<sup>3</sup> There must, therefore, be a rearrangement of the grouping of the atoms in one of the reactions.

There are three possible formulas for the product :

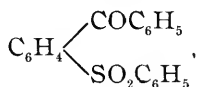
<sup>1</sup> From the author's dissertation submitted to the Board of University Studies of the Johns Hopkins University, June, 1897, for the degree of Doctor of Philosophy.

<sup>2</sup> Remsen and Dohme : *This JOURNAL*, **11**, 341; Remsen, et al. : *Ibid.*, **17**, 309; **18**, 791.

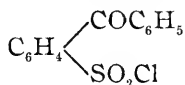
<sup>3</sup> Remsen and Saunders : *Ibid.*, **17**, 360.



From its properties and reactions its most probable structure seems to be that represented by the second formula, the phenyl residue being in combination with a carbonyl group. Remsen and Saunders<sup>1</sup> converted the chloride into the corresponding sulphonic acid by replacing the chlorine with a hydroxyl group, prepared a number of derivatives from this, and studied their properties. They also obtained a diphenyl derivative of orthosulphobenzoic acid of the formula,



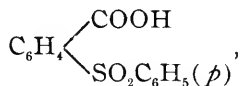
by the more prolonged action of benzene and aluminium chloride on the dichloride. The arguments which they bring forward in favor of the structure represented by the formula,



for the first product of the action are :

1. That the acid formed by the decomposition of the chloride with water is a very soluble substance, and difficult to obtain in a crystalline form.

This is characteristic of sulphonic acids in general, while, on the other hand, the corresponding carboxyl acids are much less soluble, and are easily obtainable in the form of crystals. Paraphenylsulphonebenzoic acid,



for instance, described by Newell,<sup>2</sup> is a difficultly soluble, crystalline compound. Another example will be given later in this paper.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> This JOURNAL, 20, 302.

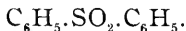


2. That the decomposition of the potassium salt by fusion with caustic potash gives benzoic acid and benzene sulphonic acid.

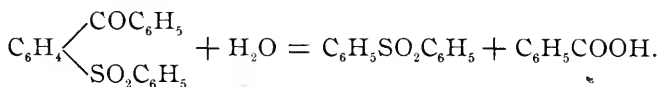
It is true that, on purely theoretical grounds, this might be a possible reaction with either of the substances represented by the formulas,



But when we come to consider the experimental evidence on the point it seems much more probable that these products would result from a compound having the first formula than one having the second. Diphenylsulphone, for instance, when fused with caustic potash, breaks down completely into diphenyl, sulphur dioxide, phenol, and various other substances.<sup>1</sup> Tollysulphone acts in a similar manner.<sup>2</sup> And these reactions take place with difficulty, showing the stability of the sulphone grouping,



The way in which the diphenyl substitution-product of orthosulphobenzoic acid breaks down also furnishes evidence in favor of this view. Remsen and Saunders found that it decomposes readily under similar circumstances into benzoic acid and diphenylsulphone,



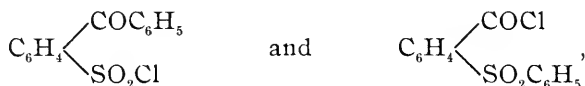
3. That the ethyl ether breaks down very readily into the acid on standing in contact with alcohol, which points to its being an ester of a sulphonic acid rather than of a carbonic acid.

4. That the chloride on treatment with ammonia, instead of forming an amide, yields a lactim. This is in accordance with the supposition that the chlorine atom left in the molecule is the one united with the sulphone group.

<sup>1</sup> Otto : Ber. d. chem. Ges., 19, 2425.

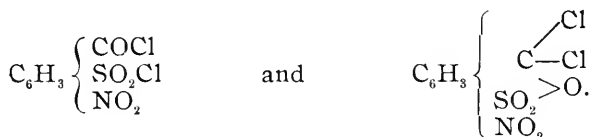
<sup>2</sup> Otto : Loc. cit.

The evidence, therefore, seems pretty clear that of the two formulas,

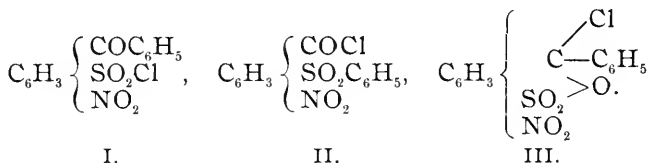


the former is the more probable for the compound obtained from the isomeric chlorides of orthosulphobenzoic acid by the Friedel and Crafts reaction with benzene.

Paranitroorthosulphobenzoic acid has also been found to yield two isomeric chlorides<sup>1</sup> by treatment with phosphorus pentachloride :



Both of these, in turn, when treated with benzene and aluminium chloride,<sup>2</sup> yield the same phenyl substitution-product having one of the three possible formulas :



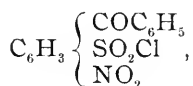
But the reaction seems in this case to stop here. No diphenyl substitution-product is formed by the further action of the reagents.

The same question arises in this case as in that of the compound just discussed : Which of the chlorine atoms is replaced by the phenyl group ? Hollis investigated the product formed and found from its properties and reactions somewhat similar evidence in favor of the first formula to that found by Remsen and Saunders in the former case. The acid obtained by decomposing the chloride with water was very soluble, and could not be obtained in the form of crystals. The ethyl ester of the acid, if one exists at all, is so unstable that it is imme-

<sup>1</sup> Remsen and Gray : *This JOURNAL*, 19, 496.

<sup>2</sup> Hollis : *Ibid.*, 23, 233.

diately transformed into the acid, when an attempt is made to prepare it from the chloride and absolute alcohol. On treating the chloride with ammonia a lactim is formed. These three reactions are perfectly analogous to those which take place with orthobenzoylbenzenesulphone chloride, under similar conditions, and point to the structure,



for the chloride. But the most conclusive evidence obtained by Remsen and Saunders for the formula which they gave, namely, the formation of certain products by fusing the acid with caustic potash, was not duplicated in the present case. The presence of the nitro group would probably make such a test less satisfactory. The evidence in this case, therefore, is not as strong as it is in that of the more simple compound.

There is, however, another method of attacking the problem by which just as conclusive evidence, but of a different kind, might be obtained. It was for the purpose of determining the nature of this evidence that the present investigation was undertaken.

If a compound having the formula,  $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{COCl} \\ \text{SO}_2\text{C}_6\text{H}_5, \\ \text{NO}_2 \end{array} \right.$  could be prepared, and its properties should be different from the compound obtained by Hollis from the isomeric chlorides of paraitroorthosulphobenzoic acid, the latter could not have the same structure, and, therefore, would probably have the formula,  $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{COC}_6\text{H}_5 \\ \text{SO}_2\text{Cl} \\ \text{NO}_2 \end{array} \right.$ . If the properties should be the same, the structure of the two would, of course, be identical.

The best method that suggested itself for preparing paranitroorthophenylsulphonecarbonyl chloride was to start with paranitrotoluene, convert it into paranitroorthotoluenesulphonic acid by treatment with fuming sulphuric acid, treat the potassium salt of this with phosphorus pentachloride to form paranitroorthotoluenesulphone chloride from which paranitroorthotoluenephenylsulphone could be made by

the Friedel and Crafts reaction with benzene. By oxidation of the methyl group in this sulphone, paranitroorthophenylsulphonebenzoic acid would be formed, and this could be transformed into paranitroorthophenylsulphonebenzoyl chloride by the action of phosphorus pentachloride.

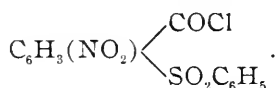
Another method which was suggested was to convert paranitrocyanbenzeneorthosulphonic acid,  $\text{C}_6\text{H}_3(\text{NO}_2)\begin{matrix} \text{CN} \\ \text{SO}_3\text{H}(o) \end{matrix}$ ,

into its chloride,  $\text{C}_6\text{H}_3(\text{NO}_2)\begin{matrix} \text{CN} \\ \text{SO}_2\text{Cl} \end{matrix}$ , replace the chlorine with

phenyl, hydrolyze the cyan group into a carboxyl group,

$\text{C}_6\text{H}_3(\text{NO}_2)\begin{matrix} \text{COOH} \\ \text{SO}_2\text{C}_6\text{H}_5 \end{matrix}$ , and treat with phosphorus pentachlo-

ride to form paranitroorthophenylsulphonebenzoyl chloride,



Positive results were not obtained by this method.

#### *Paranitroorthotoluenesulphone Chloride.*

The paranitroorthotoluenesulphone chloride, prepared according to the directions of Jensen,<sup>1</sup> formed a yellow powder, melting at 43° to 45° C., readily soluble in ether, from which it crystallized in large, rhombic crystals, melting at 44° C. (uncorr.).

Although a number of different methods were tried, none was found to yield as good results as this one. Too high a temperature, or heating too long, decreases the yield, and makes the chloride dark. The purity of the product depends largely on that of the potassium salt used. The color of the latter was found to be carried over into the chloride.

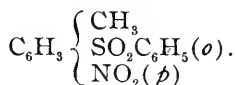
Paranitroorthotoluenesulphone chloride has been described as a liquid.<sup>2</sup> The sharp melting-point of the product obtained by the above process, and crystallized from ether, is conclusive evidence of its purity; and the existence of the

<sup>1</sup> Ann. Chem. (Liebig), **172**, 230.

<sup>2</sup> Noyes: This JOURNAL, **8**, 167.

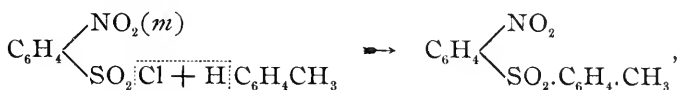
chloride in the liquid state at the ordinary temperature must be ascribed to the presence of some impurity. It is a common experience in working with solid sulphone chlorides, that the ease with which any particular specimen can be made to crystallize is much dependent on its purity.

*Paranitroorthotolylphenylsulphone,*



This was obtained from the chloride just described, by means of the Friedel and Crafts reaction with benzene.

Limpricht<sup>1</sup> obtained a compound isomeric with this, by the action of aluminium chloride and toluene on metanitrobenzenesulphone chloride,



the nitro and methyl groups being attached to different benzene rings. From the properties which are given, it seems to be quite different from paranitroorthotolylphenylsulphone, except in solubility. One of these points of difference will be taken up later under the head of the action of oxidizing agents on the sulphone.

*Preparation and Properties.*

As a preliminary experiment, 10 grams of the chloride were dissolved in about 100 cc. of benzene, in a small flask provided with a condensing tube. About 4 grams of aluminium chloride, in small pieces, were added, and the solution warmed gently. Action began slowly with the evolution of hydrochloric acid from the surface of the aluminium chloride. The solution began to darken quickly, and, after heating for five minutes, the action was stopped by cooling the flask, and the contents were poured into dilute hydrochloric acid. The benzene solution was then separated from the water and evaporated to dryness. The residue—a dark-brown, tarry mass—was treated in different portions with alcohol, ether, chloro-

<sup>1</sup> Ann. Chem. (Liebig), 278, 257.

form, and benzene, and the solutions filtered. Crystals separated from each of the solutions on evaporation, but the ether and alcohol dissolved less of the dark tarry substance, and consequently furnished the best crystals.

It was found, on further experimenting, that the aluminium chloride reacted more satisfactorily when powdered, and that it was not necessary to use such a large proportion of benzene. The darkening, which takes place rapidly after the action begins, could not be prevented, and it was found to have less effect on the final product than was at first supposed.

Previously to using the method finally adopted the yield was small, only 6 grams of the sulphone being obtained from 35 grams of the chloride. This method is similar to that used by Beckurts and Otto<sup>1</sup> in preparing paratolylphenylsulphone from benzenesulphone chloride and toluene, and by Newell<sup>2</sup> in making the same substance from paratoluenesulphone chloride and benzene. Only 20 grams of the chloride were used at a time, as this was found to give the best results. It was dissolved in an equal weight of warm benzene in a flask connected with a condensing tube. The solution was placed on a water-bath and heated so that the benzene solution boiled gently. Fifteen grams of powdered aluminium chloride were added gradually, 3 or 4 grams at a time—the violent action being allowed to subside after each addition. The solution was heated for half an hour, allowed to cool, poured into a liter of water containing 20 to 30 cc. of concentrated hydrochloric acid. A voluminous light-brown, flocculent precipitate formed. The solution was warmed on the water-bath until all of the benzene had evaporated, the precipitate filtered off, and drained with the filter-pump. This process was repeated until 200 grams of the chloride had been used. Most of the precipitate was found to be soluble in alcohol, but the yield was considerably decreased in the process of purification.

The collected residues were extracted with hot alcohol, and the alcoholic solution boiled with animal charcoal until nearly colorless, and filtered while hot with the use of a hot-water funnel. The marked difference in the solubility of the sul-

<sup>1</sup> Ber. d. chem. Ges., **11**, 2068.

<sup>2</sup> *Loc. cit.*

phone in hot and cold alcohol caused considerable difficulty in its purification. Most of it crystallized out from the alcohol on cooling, in the form of thin, silver-white plates, melting at  $158^{\circ}$  C. (uncorr.). That which remained dissolved in the cold alcohol was obtained by concentrating the solution. This part of the product was not as pure as that which separated out from the original solution, as it was found that an alcoholic solution of the sulphone became brown when boiled for a while, or even allowed to stand at the ordinary temperature for more than a day. The charcoal took up a considerable amount of the sulphone, which was recovered by extracting with alcohol.

Analysis of the product gave the following results :

- I. 0.3140 gram substance gave 0.2652 gram  $\text{BaSO}_4$ .
- II. 0.1583 gram substance gave 0.1356 gram  $\text{BaSO}_4$ .
- III. 0.2863 gram substance gave 0.5934 gram  $\text{CO}_2$ , and 0.1058 gram  $\text{H}_2\text{O}$ .
- IV. 0.2994 gram substance gave 0.6201 gram  $\text{CO}_2$ , and 0.1063 gram  $\text{H}_2\text{O}$ .
- V. 0.3229 gram substance gave 0.017 gram N.

	Calculated for $\text{C}_{13}\text{H}_{11}\text{O}_4\text{NS}$ .	I.	II.	Found. III.	IV.	V.
C	56.30	....	....	56.56	56.52	....
H	4.00	....	....	4.13	3.93	....
S	11.56	11.60	11.76	....	....	....
N	5.06	....	....	....	....	5.26

Paranitroorthotolylphenylsulphone exhibits, in a marked degree, the general stability of sulphones toward concentrated acids. It is, however, much less stable toward alkalis than the simpler sulphones, undoubtedly on account of the presence of the nitro group. Most of the ordinary organic solvents dissolve it easily.

It was found to be nearly as soluble in methyl alcohol as in ethyl alcohol. Benzene and acetone dissolve it very readily, and it crystallizes out from both in plates, which, in the latter case, are very narrow, and to the naked eye have the appearance of needles. It is almost equally soluble in hot and cold ether, and to rather a small extent. Hot ligroin dissolves it with ease. In water it is practically insoluble, even in boil-

ing water ; but that it does dissolve to a limited extent is shown by the fact that the filtrate from a water solution gives a faint yellow color when boiled with a solution of caustic potash. This is a very delicate test, as one small crystal of the sulphone, dissolved in alcohol, gives a distinct red color with such a solution.

Dilute nitric and sulphuric acids dissolve the sulphone in small amounts ; dilute hydrochloric acid does not dissolve it. Concentrated nitric and sulphuric acids dissolve it quite appreciably in the cold, and give it up again on dilution with water. A small amount was boiled with concentrated nitric acid for five minutes, the solution cooled, and diluted with water. The sulphone was precipitated in crystalline form, and it melted sharply at  $158^{\circ}\text{C.}$ , showing that it had not been acted upon by the acid. A similar experiment was tried with fuming nitric acid, with the same result. A mixture of equal parts by volume of concentrated nitric and sulphuric acids was then tried ; the sulphone which crystallized out on dilution had a sharp melting-point. When boiled with a mixture of concentrated sulphuric and fuming nitric acids it was slightly decomposed. There was no apparent action, but the white precipitate which formed on dilution did not melt sharply.

The sulphone dissolved quite readily in ordinary concentrated sulphuric acid in the cold, and was precipitated unchanged when the solution was poured into water. When the acid was warmed to  $100^{\circ}\text{C.}$  the solubility of the sulphone increased, but it was not acted upon. When the temperature was raised much above this the sulphone was decomposed, as shown by the charring. Fuming sulphuric acid dissolved the sulphone easily, and it was not precipitated on dilution.

#### *Action of Fuming Sulphuric Acid.*

When the sulphone is treated with fuming sulphuric acid it is converted into a sulphonic acid. An analysis of the barium salt of this acid is here given :

0.0849 gram substance lost 0.0097 gram at  $150^{\circ}\text{C.}$ , and gave 0.0209 gram  $\text{BaSO}_4$ .

	Calculated for $(\text{C}_{13}\text{H}_{10}\text{O}_7\text{S}_2\text{N})_2\text{Ba} + 6\text{H}_2\text{O}.$	Calculated for $(\text{C}_{13}\text{H}_{10}\text{O}_7\text{S}_2\text{N})_2\text{Ba}.$	Found.
$\text{H}_2\text{O}$	11.28	....	11.42
Ba	....	16.16	16.35



*Action of Potassium Hydroxide.*

A mere trace of the sulphone in solution gives a purplish-red color with caustic potash.

A few crystals of the sulphone were dissolved in alcohol and the solution of caustic potash added. Upon being heated the solution quickly assumed a deep purple color, which became red after boiling for a while, and finally a purplish-red precipitate formed. Dilute hydrochloric, nitric, and sulphuric acids were added to different portions of the solution. They changed the color to reddish-yellow, and the purple color was restored on addition of excess of potassium hydroxide. The purple color was not brought back, however, with either ammonium hydrate or sodium carbonate. Concentrated sulphuric, nitric, and hydrochloric acids each produced apparently the same result as the dilute acids. But when the solutions were made alkaline again with caustic potash, the purple color did not return. The purple-colored compound was evidently decomposed by the concentrated acids.

Caustic soda had the same effect on the sulphone as caustic potash. Ammonium hydrate and sodium carbonate had no action on the sulphone.

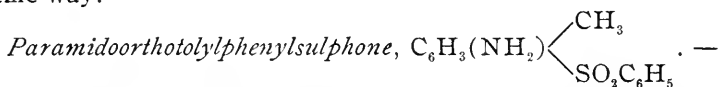
An attempt was made to isolate the compound formed. About 5 grams of the sulphone were dissolved in absolute alcohol, and treated with an alcoholic solution of pure potassium hydroxide. The solution was boiled for five minutes, cooled, and poured into about a liter of water. A red flocculent precipitate settled to the bottom of the vessel, leaving the supernatant liquid clear and not very deeply colored. The precipitate was washed by decantation until no longer alkaline, then boiled with water and washed again. After filtering off and drying, its solubility in a number of solvents was tried for the purpose of finding a method for purifying it. Treated with alcohol, ether, acetone, and acetic acid, it gave a slight red color to each, but did not dissolve appreciably. Evaporation of the solutions in each case left but a trace of amorphous residue. Concentrated sulphuric acid dissolves it to a certain extent, forming a deep purple-colored solution. On diluting, the color changed to reddish-yellow, and the

original purple color did not appear again, on making the solution alkaline with potassium hydroxide. The substance left quite a large amount of ash when ignited, consisting evidently of the potassium hydroxide that could not be removed by washing. On account of its insolubility the substance could not be obtained pure.

*Action of Reducing Agents :—Ammonium Sulphide.*

Gericke<sup>1</sup> found that when nitrophenylsulphone in alcoholic solution is treated with ammonium sulphide and heated it is reduced to amidophenylsulphone. Noyes<sup>2</sup> has shown also that paranitroorthosulphobenzoic acid is easily reduced by the same reagent to paramidoorthosulphobenzoic acid.

The nitro group of paranitroorthotolylphenylsulphone was also found to be readily converted into an amido group in the same way.



Four grams of paranitroorthotolylphenylsulphone were dissolved in 100 cc. of hot alcohol, about 20 cc. of concentrated ammonia water added, and sulphuretted hydrogen passed into the solution for fifteen minutes. The solution became blood-red in a short time. A small amount of the solution was removed and treated with water, which caused a voluminous precipitate of short, needle-shaped crystals. The main portion of the solution was then evaporated to dryness on a water-bath, and the residue digested with water containing a small amount of hydrochloric acid. The portion remaining undissolved, which consisted of sulphur, was removed by filtration through a layer of flowers of sulphur in a Gooch crucible. On making the filtrate alkaline with caustic soda, a heavy white precipitate came down. This was filtered off, washed, and drained with the filter-pump. It was then dissolved in alcohol, treated with animal charcoal, boiled, filtered, and allowed to crystallize out. The crystals were large, thin, irregular-shaped, colorless plates, and melted at 156° C. (uncorr.). They were difficultly soluble in hot water, and crys-

<sup>1</sup> Ann. Chem. (Liebig), 100, 208.

<sup>2</sup> This JOURNAL, 8, 167.

tallized out from this solution in very small plates. Alcohol and acetone dissolved them readily, and they were not precipitated from either solution on addition of water. They dissolved to only a small extent in either cold or boiling ether. Benzene dissolved them very readily, and the compound crystallized out in the form of needles.

I. 0.1681 gram substance gave 8 cc. N at 19° C., and 765 mm. Hg pressure = 0.009264 gram.

II. 0.3496 gram substance gave 17.5 cc. N at 20° C., and 755 mm. Hg pressure = 0.0199 gram.

	Calculated for $C_{13}H_{13}O_2NS$ .	I.	Found. II.
N	5.67	5.51	5.69

*Action of Oxidizing Agents.*

1. *Chromic Acid*.—Newell<sup>1</sup> found that the best method for converting paratolylphenylsulphone into paraphenylsulphone-benzoic acid, is by treatment with chromic acid in glacial acetic acid solution. The same method was tried with this sulphone.

Ten grams of the sulphone were dissolved in glacial acetic acid and heated to boiling in a flask provided with a return condenser. A saturated solution of about 12 grams of chromic acid in glacial acetic acid was added, in small quantities at a time, the solution being kept just hot enough to boil gently. After all the chromic acid had been added, the solution was boiled for three hours. It was filtered and the acetic acid evaporated from the filtrate. The original precipitate was found to consist of chromic oxide, almost free from organic matter. The residue from the filtrate consisted principally of unaltered sulphone mixed with the chromic acid that remained.

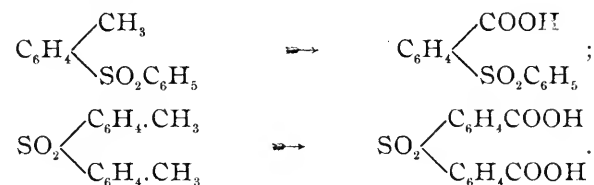
The action of chromic acid in this case, or rather its lack of action, is in accord with its usual behavior toward ortho substitution-products of toluene. The presence of the phenylsulphone group,  $SO_2C_6H_5$ , in the ortho position to the methyl group, seems to shield the latter from the action of chromic acid.

2. *Potassium Permanganate*.—The most efficient oxidizing agent for the ortho-substituted toluenes has generally been

<sup>1</sup> *Loc. cit.*

found to be potassium permanganate in water solution.

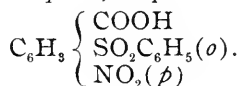
The action of oxidizing agents on sulphones was first investigated by R. Otto. He found<sup>1</sup> that when diphenyl sulphone, mixed with water acidified with sulphuric acid, is treated with potassium permanganate, the permanganate is somewhat reduced, as shown by the precipitation of manganese dioxide. Michael and Adair<sup>2</sup> showed later that tolylphenylsulphone and ditolylsulphone are oxidized by potassium permanganate to a phenylsulphonebenzoic acid and a phenylsulphonedibenzoic acid, respectively :



When the reaction was carried on in acetic acid solution the yield was small. A water solution of potassium permanganate gave much better results, although the sulphone was but little soluble in water, and only half of it was oxidized by the theoretical quantity of potassium permanganate.

Paranitroorthotolylphenylsulphone was found to act in a similar manner.

*Paranitroorthophenylsulphonebenzoic Acid,*



The acid was prepared by the following method :

Ten grams of the sulphone were suspended in a liter of water in a 1.5 liter flask. The sulphone had previously been powdered as fine as possible in a mortar. A solution of 30 grams of potassium permanganate was added, one-quarter at a time, at intervals of an hour, to the solution which was heated to boiling meanwhile on a sand-bath. The color of the permanganate was gradually displaced by that of the manganese dioxide as the reaction progressed. It was difficult to determine, from the appearance of the solution, when the last

<sup>1</sup> Ann. Chem. (Liebig), **145**, 37.

<sup>2</sup> Ber. d. chem. Ges., **11**, 119.

traces of the permanganate had disappeared, without letting the solution settle, which required considerable time. A small amount of the solution was removed occasionally and filtered, and when a colorless filtrate was obtained the heating was stopped. It usually required eight hours to decompose all of the potassium permanganate. The solution was allowed to cool, and filtered. On acidifying the filtrate with hydrochloric acid a finely divided, white precipitate came down, and, on standing, it collected in masses of irregular, needle-shaped crystals. It was filtered off and purified by redissolving it in water, and treating with animal charcoal. The largest yield obtained at one time was 2.8 grams of the acid from 10 grams of the sulphone. A considerable amount of sulphone was always left unacted upon, and mixed with the precipitate of manganese dioxide. It was recovered by dissolving the dioxide in concentrated hydrochloric acid and filtering off the undissolved sulphone, which was not attacked by the nascent chlorine.

Paranitroorthophenylsulphonebenzoic acid crystallizes in white needles 5 to 10 mm. long, melting at  $196^{\circ}$  C. (uncorr.). It is difficultly soluble in cold water, and not very readily in hot water. It has a bitter-sweet taste. Acetone dissolves it readily, but ether and benzene only to a small extent.

*Barium nitrophenylsulphonebenzoate*,  $(\text{C}_6\text{H}_3\text{NO}_2\text{SO}_2\text{C}_6\text{H}_5\text{COO})_2\text{Ba} \cdot \text{H}_2\text{O}$ , crystallizes in the form of short, white needles, matted together, and difficultly soluble in hot water. Analysis gave the following results:

I. 0.3784 gram substance lost 0.0100 gram at  $178^{\circ}$  C., and gave 0.1146 gram  $\text{BaSO}_4$ .

II. 0.5043 gram substance lost 0.0125 gram at  $178^{\circ}$  C., and gave 0.1524 gram  $\text{BaSO}_4$ .

	Calculated for $(\text{C}_{13}\text{H}_5\text{O}_6\text{NS})_2\text{Ba} \cdot \text{H}_2\text{O}$ .	Calculated for $(\text{C}_{13}\text{H}_5\text{O}_6\text{NS})_2\text{Ba}$ .	I.	Found. II.
$\text{H}_2\text{O}$	2.34	....	2.64	2.48
Ba	....	18.32	18.30	18.23

*Calcium nitrophenylsulphonebenzoate*,  $(\text{C}_6\text{H}_3\text{NO}_2\text{C}_6\text{H}_5\text{COO})_2\text{Ca} \cdot 6\frac{1}{2}\text{H}_2\text{O}$ , crystallizes in tufts of radiating, colorless, prismatic, crystals, easily soluble in hot water. Analysis of the salt gave the following results:

0.1907 gram substance lost 0.0292 gram at 160° C., and gave 0.0342 gram  $\text{CaSO}_4$ .

	Calculated for ( $\text{C}_{13}\text{H}_8\text{O}_6\text{NS}$ ) <sub>2</sub> Ca.H <sub>2</sub> O.	Calculated for ( $\text{C}_{13}\text{H}_8\text{O}_6\text{NS}$ ) <sub>2</sub> Ca.	Found.
H <sub>2</sub> O	15.21	....	15.31
Ca	....	6.14	6.23

*Comparison of Paranitroorthophenylsulphonebenzoic Acid with Paranitroorthobenzoylbenzenesulphonic Acid.*

Hollis<sup>1</sup> found that the acid formed by the action of water and dilute acids on the product of the Friedel and Crafts reaction with the chlorides of paranitroorthosulphobenzoic acid, is very easily soluble in water, and cannot be obtained in crystallized form. Its barium salt crystallizes with varying amounts of water of crystallization, but never with less than 3 molecules. The crystals have the form of tufts of radiating needles or monoclinic prisms. Its calcium salt crystallizes in thin plates with 3 molecules of water of crystallization.

Paranitroorthophenylsulphonebenzoic acid, on the other hand, is difficultly soluble in water and crystallizes easily. Its barium salt crystallizes as short needles, matted together, and containing 1 molecule of water of crystallization; and its calcium salt crystallizes in prisms containing 6.5 molecules of water of crystallization.

The difference can be brought out more strikingly by means of the following table:

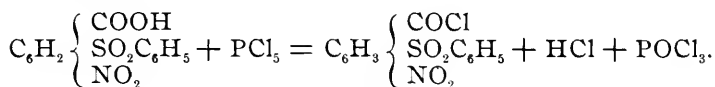
<i>Paranitroorthobenzoylbenzenesulphonic Acid.</i>	<i>Paranitroorthophenylsulphonebenzoic Acid.</i>
Very soluble in water.	Difficultly soluble in water.
Not crystallizable.	Crystallizes easily.
Barium salt contains from 3 to 7 molecules of water of crystallization, and crystallizes in tufts of radiating needles or monoclinic prisms.	Barium salt contains 1 molecule of water of crystallization, and crystallizes in short, matted needles.
Calcium salt crystallizes in plates with 3 molecules of water of crystallization.	Calcium salt crystallizes in prisms with 6.5 molecules of water of crystallization.

<sup>1</sup> *Loc. cit.*

*Action of Phosphorus Pentachloride on Paranitroorthophenylsulphonebenzoic Acid.*

Phosphorus pentachloride acts readily on the free acid, to form paranitroorthophenylsulphonebenzoyl chloride.

When the acid was intimately mixed with phosphorus pentachloride, free from oxychloride, no action was noticed until the temperature was raised to 160° C. But when the pentachloride contained phosphorus oxychloride, the reaction began immediately at the ordinary temperature on mixing the two together. The reaction which takes place may be represented thus :



*Paranitroorthophenylsulphonebenzoyl Chloride.*

Equal weights of paranitroorthophenylsulphonebenzoic acid and phosphorus pentachloride containing a small amount of the oxychloride were intimately mixed in a mortar. The mixture gradually softened into a semiliquid mass, with rise of temperature, and liberation of hydrochloric acid and phosphorus oxychloride. After the action was over the mass was transferred to an evaporating dish and heated about ten minutes longer at about 150° C. It then had the appearance of a light-brown, transparent liquid. It was allowed to cool to the ordinary temperature, and washed with cold water, which caused it to solidify to a light-yellow, granular solid. It was reduced to a fine powder and washed until free from phosphoric acid, dried with drying-paper, and dissolved in warm chloroform. It crystallized out of the solution on the spontaneous evaporation of the chloroform, as well-formed, colorless, rhombic crystals, from 1 to 5 mm. long, melting at 109° C. (uncorr.). The crystals were easily soluble in chloroform, ether, benzene, and ligroin.

The chlorine in the chloride was determined by boiling with a dilute solution of pure caustic soda (made from metallic sodium), acidifying with nitric acid, and precipitating with silver nitrate.

- I. 0.1631 gram substance gave 0.0716 gram AgCl.  
 II. 0.1847 gram substance gave 0.0810 gram AgCl.

	Calculated for $C_{13}H_8O_6NSCl$ .	I.	Found.	II.
Cl	10.88	10.85		10.84

*Action of Water.*

The chloride is quite stable in the presence of water at ordinary temperatures. No change could be detected in crystals which remained in contact with water several days. But it is readily decomposed when boiled with water.

Dilute caustic alkalis in solution decompose the chloride much more quickly than water. Two-tenths gram of the chloride was entirely decomposed when boiled with a very dilute solution of caustic potash for five minutes. Hydrochloric acid was added in excess to the solution, and very fine, needle-shaped crystals separated out on cooling. Their melting-point,  $196^{\circ}$  C., showed them to be paranitroorthophenylsulphonebenzoic acid.

*Action of Ammonia.*

By the action of ammonia the chlorine of the carbonyl chloride group is replaced by an amido residue.

Some of the finely powdered chloride was added to a dilute solution of ammonia in a flask and allowed to remain in contact with it for several days. The solid material in the bottom of the flask at the end of this time had the same appearance as the chloride—a light-yellow powder. The ammonia was evaporated off on a water-bath, and the solution filtered from the residue, which was washed, dried, and dissolved in hot chloroform, in which it was not very readily soluble. When the chloroform evaporated, it crystallized out in well-formed, colorless, prismatic crystals, apparently monoclinic, and melting at  $191^{\circ}$  to  $192^{\circ}$  C. (uncorr.). The crystals were analyzed with the following results:

- I. 0.4049 gram substance gave 0.3004 gram  $BaSO_4$ .  
 II. 0.1515 gram substance gave 0.01385 gram N.

	Calculated for $C_{13}H_{10}O_6N_2S$ .	I.	Found.	II.
S	10.46	10.19		....
N	9.16	....		9.14



The product is

*Paranitroorthophenylsulphonebenzamide.*—The amide is practically insoluble in water, benzene, and ether. It dissolves readily in hot alcohol, and crystallizes out as the solution cools, in the form of prisms. Acetone also dissolves it very easily, and well-formed prisms crystallize out on evaporation of the acetone.

*Action of Benzene and Aluminium Chloride.*

On adding aluminium chloride to a warm solution of the orthosulphonebenzoyl chloride in benzene, a slight evolution of hydrochloric acid took place, and a brown, tarry mass, which was insoluble in the benzene, very soon collected around the aluminium chloride and prevented further action.

Two grams of the chloride were dissolved in about 10 grams of benzene, and 2 grams of powdered aluminium chloride added. The solution was heated on a water-bath until it just began to boil, and it was then kept at this temperature. Hydrochloric acid was given off quite rapidly at first, passing out in a continuous stream from the condensing-tube. After the evolution of acid had ceased, the solution was cooled and poured into water. The mixture was heated on the water-bath until the benzene had evaporated. The tarry mass which remained at the bottom of the beaker was found to be insoluble in benzene, alcohol, ether, chloroform, and acids. It did not, therefore, lend itself to further investigation.

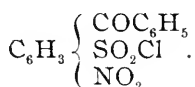
Lack of material prevented the carrying out of any more experiments of this kind.

*Comparison of Paranitroorthophenylsulphonebenzoyl Chloride with Paranitroorthobenzoylbenzenesulphone Chloride.*

The compound obtained by Hollis<sup>1</sup> from the action of benzene and aluminium chloride on the isomeric chlorides of paranitroorthosulphobenzoic acid, crystallizes from its solution in benzene in the form of purple or green monoclinic crystals, melting at 177° C. It yields a non-crystallizable acid when boiled with water, and when treated with ammonia it combines with it, with the loss of hydrochloric acid and water, to

<sup>1</sup> *Loc. cit.*

form a lactim which melts at  $234^{\circ}\text{C.}$ , and which is not very soluble in alcohol. Its reactions, therefore, are in accordance with what we should expect from a compound having the formula,



Paranitroorthophenylsulphonebenzoyl chloride, isomeric with the above compound, crystallizes from benzene in colorless or light-yellow, rhombic crystals, melting at  $109^{\circ}\text{C.}$  When boiled with water, it forms a well-crystallized acid, which melts at  $196^{\circ}\text{C.}$ ; and it reacts with ammonia to form an amide crystallizing in prisms which melt at  $191^{\circ}$  to  $192^{\circ}\text{C.}$ , and are readily soluble in alcohol. These properties characterize it as quite distinct from the compound of the same empirical composition described above.

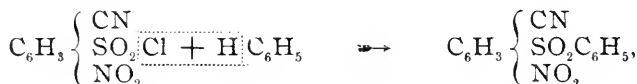
*An Attempt to Transform Paranitroorthocyanbenzenesulphonic Acid into Paranitroorthophenylsulphonebenzoic Acid.*

The unsymmetrical chloride of paranitroorthosulphobenzoic acid is converted into the ammonium salt of paranitroorthocyanbenzenesulphonic acid,  $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CN} \\ \text{SO}_2\text{ONH}_4 \\ \text{NO}_2 \end{array} \right.$ , when treated

with a solution of ammonia. It was thought that this substance might furnish the starting-point for another method for the preparation of paranitroorthophenylsulphonebenzoic acid. By the action of phosphorus pentachloride on the potassium salt of this acid, paranitroorthocyanbenzenesulphone chloride,

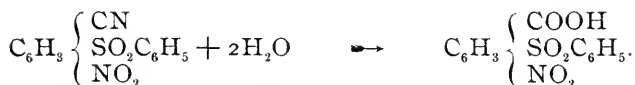
$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CN} \\ \text{SO}_2\text{Cl} \\ \text{NO}_2 \end{array} \right.$ , is formed.<sup>1</sup> It was hoped that by the action of

benzene and aluminium chloride this would yield paranitroorthocyanodiphenylsulphone according to the reaction,



which, by hydrolysis of the cyan residue, would give paranitroorthophenylsulphonebenzoic acid,

<sup>1</sup> Remsen and Gray : This JOURNAL, 19, 510.



The material for the experiments was prepared by Mr. W. E. Henderson, of this laboratory. The ammonium salt, which was obtained as a waste-product in the preparation of the symmetrical chloride of paranitroorthosulphobenzoic acid, was converted into the potassium salt by adding caustic potash or potassium chloride to its solution in hot water. The potassium salt is difficultly soluble in cold water, and separates out in the form of needles as the solution cools. Potassium chloride was found to work more satisfactorily than potassium hydrate. An analysis by Mr. Henderson of the potassium salt prepared in this way confirmed its purity. The salt was heated two or three hours in an air-bath at about 130° C. to free it from water of crystallization.

Twenty-five grams of the dry potassium salt were mixed in a mortar with an equal weight of phosphorus pentachloride, placed in an evaporating dish, and heated to 140° C. on a sulphuric-acid bath. After the reaction had ceased, the heating was continued half an hour longer to evaporate off the phosphorus oxychloride. It was allowed to cool to the ordinary temperature and treated with cold water, which caused it to solidify. It was ground to a fine powder, washed several times with water, drained, and dissolved in chloroform. A small portion remained undissolved, which was probably the anhydride of the acid. Some of the acid was also recovered from the water used in washing the chloride, showing that the use of a larger quantity of phosphorus pentachloride is necessary to convert all of the potassium salt into the chloride. The chloroform solution was freed from water by calcium chloride, and allowed to evaporate spontaneously. Large, well-formed, quadrilateral, prismatic crystals were obtained, which melted at 104°.5 to 105°.5 C. (uncorr.).

Ten grams of the chloride were dissolved in an equal weight of warm benzene, in a flask provided with a condensing-tube, and 8 grams of powdered aluminium chloride added gradually, in small portions at a time. No reaction took place until the solution was warmed. A brown, tarry mass then collected at

the bottom of the flask, forming a solid cake with the aluminium chloride. The solution was heated on the water-bath until hydrochloric acid was no longer given off. Although considerable hydrochloric acid was liberated, there was no apparent evolution from the surface of the aluminium chloride, as is usually the case in the Friedel and Crafts reaction. The benzene solution, which had a slight-brown color, was poured into water, and the mixture heated on the water-bath until the benzene had all evaporated. Nothing remained in the water but a small amount of undecomposed chloride. The residue in the flask was washed with dilute hydrochloric acid and extracted with alcohol. That which remained undissolved in the alcohol was a brown, amorphous powder, insoluble in ether, benzene, chloroform, and concentrated acids. The alcoholic extract was evaporated to dryness on the water-bath, leaving a brown, tarry mass, from which no crystalline product could be obtained. It was dissolved in ether, chloroform, benzene, and acetone, but separated out in the same form on evaporation of the solutions.

The experiment was repeated with 100 cc. of benzene and 10 grams of the chloride, and the result was essentially the same.

The presence of the cyan group evidently interferes with the action of benzene on the sulphone chloride residue.

### *Conclusions.*

The results of this investigation lead to the following conclusions :

1. Paranitroorthotolylphenylsulphone can be readily obtained by the action of benzene and aluminium chloride on paranitroorthotoluenesulphone chloride.
2. This sulphone has the general properties of aromatic sulphones, and certain other properties due to the presence of the nitro group.
3. Paranitroorthotolylphenylsulphone is oxidized by potassium permanganate in neutral solution to paranitroorthophenylsulphonebenzoic acid, and this acid is quite different in properties from the isomeric compound obtained by decomposing with water, the product of the action of benzene and

aluminium chloride on the chlorides of paranitroorthosulphobenzoic acid.

4. Paranitroorthophenylsulphonebenzoic acid passes over quantitatively into paranitroorthophenylsulphonebenzoyl chloride when treated with phosphorus pentachloride.

5. Paranitroorthophenylsulphonebenzoyl chloride has perfectly definite properties, which distinguish it from the isomeric compound obtained by the action of benzene and aluminium chloride on the chlorides of paranitroorthosulphobenzoic acid. Among other differences, attention is called to the fact that it forms an amide with ammonia, while the latter forms a lactim.

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## CONCERNING LIPASE, THE FAT-SPLITTING ENZYME, AND THE REVERSIBILITY OF ITS ACTION.

BY J. H. KASTLE AND A. S. LOEVENHART.

It was suggested by one of us (Loevenhart) that possibly lipase might be capable of effecting the synthesis of fats from fatty acid and glycerin as well as their hydrolysis into these products. It was with the view of making an experimental study of this question that this investigation was first undertaken. An examination of the literature of the subject revealed that but comparatively little was known concerning the fat-splitting enzyme. It was therefore deemed advisable to extend the original scope of the investigation. The most convenient source of the enzyme to us was the pancreas of the pig. In the preparation of our extracts, the organ was removed from the animal within thirty minutes after death, dissected as free as possible from fat, thoroughly macerated with coarse white sand, and extracted with water or glycerin. It was afterwards found more convenient, however, to cut up the pancreas in small pieces upon its removal from the animal, and preserve it in chloroform water in cold storage until required for use. At first the activity of the enzyme was tested upon pure butter-fat, litmus being used as the indicator and the time being noted that was required

to pass from the blue color to a definite shade of red. Under the best conditions, however, lipase hydrolyzes the fats but slowly, and hence they are by no means convenient substances with which to follow the change in question. In testing the activity of the pancreas extract on other ethereal salts, it was observed that it hydrolyzed ethyl butyrate comparatively rapidly, and, except where expressly stated to the contrary, this ethereal salt was employed in all of our experiments. Ethyl butyrate further possesses the advantage that the amount split by water alone at the temperature at which we worked, is not measurable within the duration of our experiments. The experiments were carried out in test-tubes usually in the following manner: 4 cc. of water, 0.1 cc. toluene (as antiseptic), and 0.26 cc. ethyl butyrate<sup>1</sup> were placed in test-tubes. The tubes were then tightly corked and heated to the desired temperature, usually 40°, for five minutes, to bring their contents to the temperature of the bath, at the end of which time 1 cc. of the enzyme solution was added to each. The tube was then heated for the desired time, usually for fifteen minutes, when it was removed from the bath, plunged into ice-water, and titrated with N/20 KOH, neutral litmus being used as the indicator. In what follows, the initial acidity of the enzyme solution, usually amounting to 0.1 to 0.2 cc. N/20 KOH, has in every case been deducted from the cubic centimeters KOH required.

That the hydrolysis of ethyl butyrate and other ethereal salts was in reality brought about by the action of an enzyme, and not by other agents, was proved by numerous control experiments in which the solution of the enzyme was boiled before it was used. It may be of interest to note in this connection that in not a single instance did the control experiment show any hydrolysis of the ethereal salt.

The action of fat-splitting bacteria was prevented by antiseptics, usually toluene or thymol.

In our early experiments no special attention was paid to the amount of pancreas employed in the preparation of the extracts. It soon became manifest, however, that it would be

<sup>1</sup> At 30° C. (summer temperature) 0.26 cc. ethyl butyrate weighs 0.2300 gram. This quantity, if completely hydrolyzed, would require 39.7 cc. N/20 KOH. These numbers are employed in the following in calculating the amount of hydrolysis.

far better, for purposes of comparison at least, to employ definite amounts of the gland, and hence it will be observed in what follows that 10, 20, and even 50 per cent extracts were used. By this is meant that 10, 20, or 50 grams of gland were extracted with water and made up to 100 cc.

Several other tissues of the pig have been found to exhibit lipolytic activity towards ethyl butyrate, notably the liver, the submaxillary gland, and the kidney. A comparison of the lipolytic activity of 10 per cent extracts of these tissues has been made in the following manner: Tubes were prepared containing 4 cc. of water, 0.1 cc. toluene, and 0.26 cc. ethyl butyrate. These were then heated for five minutes at 40° when 1 cc. of the extract to be tested was added. The enzyme was allowed to act for forty minutes, at the end of which time the solution was titrated with N/20 KOH. The following were the results obtained:

	cc. N/20 KOH required.	Per cent of hydrolysis.
Pancreas	1.4	3.52
Kidney	0.7	1.76
Liver	4.1	10.29
Submaxillary gland	0.5	1.26

Taking the extract of the pancreas as unity, the lipolytic activity of the other tissues of the pig stand in the following ratio:

Pancreas	1.0
Liver	2.93
Kidney	0.50
Submaxillary gland	0.36

The liver of the pig showed such remarkable lipolytic activity that it occurred to us to compare it with the liver of certain other animals in this respect. Livers of the pig, beef, sheep, chicken, and duck were obtained in fresh condition in the market. Ten per cent aqueous extracts of these were prepared, and their activity toward ethyl butyrate tested in the manner already described.

Duration of experiments, fifteen minutes; temperature, 40°; antiseptic, toluene.

		cc. N/20 KOH required.	Per cent of hydrolysis.
Pig	liver	3.45	8.66
Sheep	"	1.90	4.77
Duck	"	1.075	2.70
Beef	"	0.875	2.20
Chicken	"	0.775	1.95

Another interesting occurrence of lipase has been observed in the stomach of the pig. It has long been known that fats are hydrolyzed to some extent in the stomach.<sup>1</sup> The exact cause of this, however, seems not to have been determined with certainty. By some it is believed to be brought about by bacteria in the early stages of gastric digestion.<sup>2</sup> In order to test this point, 25 grams of the mucous membrane of the pig's stomach were ground with coarse sand, and water added. The extract was strained through linen cloth and made up to 100 cc. A small quantity of toluene was added as the antiseptic. This extract was found to possess lipolytic activity in neutral solutions. It was found to be rendered permanently inactive, however, by free hydrochloric acid in about the quantity normally present in gastric juice. These facts are brought out in the following experiments :

In the first series of experiments three solutions were employed, labeled A, B, and C, respectively. Solution A contained 5 cc. of 0.6 per cent hydrochloric acid, and 5 cc. of the active extract of the pig's stomach. The hydrochloric acid was, therefore, acting in a concentration of 0.3 per cent.

Solution B contained 5 cc. of the active extract of the pig's stomach and 5 cc. of water. Solution C contained 5 cc. of hydrochloric acid of 0.6 per cent and 5 cc. of water.

#### *Experiments (First Series).*

Time, 30 minutes ; temperature, 40°.

- (1) 1 cc. solution A ; 4 cc. water ; 0.1 cc. toluene ; 0.26 cc. ethyl butyrate.

Increase in acidity = 0.05 cc. N/20 KOH = 0.13 per cent hydrolysis.

<sup>1</sup> Marcet: Proc. Roy. Soc., 9, 306 (1858) ; Ogata : Du Bois Arch., 515 (1881) ; Cash : Arch. f. Anat. u. Physiol., 1880, S. 323.

<sup>2</sup> Schäfer : "Text-book of Physiology," Vol. I, p.443 (1898).



- (2) A duplicate experiment of above (No. 1) gave the same result. This slight hydrolysis was due to the hydrochloric acid present, see Exp. 4.
- (3) 1 cc. of solution B ; 4 cc. water ; 0.1 cc. toluene ; 0.26 cc. ethyl butyrate.  
Increase in acidity = 0.25 cc. N/20 KOH = 0.64 per cent hydrolysis.
- (4) 1 cc. solution C ; 4 cc. water ; 0.1 cc. toluene ; 0.26 cc. ethyl butyrate.  
Increase in acidity = 0.05 cc. N/20 KOH, decomposition 0.13 per cent.

*Experiments (Second Series).*

Time, thirty minutes ; temperature, 40° C.

- (1) 2 cc. extract of pig's stomach (boiled) ; 2 cc. water ; 0.1 cc. toluene ; 0.26 cc. ethyl butyrate.  
Increase in acidity 0.1 cc. N/20 KOH ; decomposition 0.25 per cent.
- (2) 2 cc. extract pig's stomach (boiled) ; 2 cc. 0.6 per cent hydrochloric acid ; 0.1 cc. toluene ; 0.26 cc. ethyl butyrate.  
Increase in acidity 0.2 cc. N/20 KOH ; decomposition 0.5 per cent.
- (3) 2 cc. active extract of pig's stomach ; 2 cc. 0.6 per cent hydrochloric acid ; 0.1 cc. toluene ; 0.26 cc. ethyl butyrate.  
Increase in acidity 0.1 cc. N/20 KOH ; decomposition 0.25 per cent.
- (4) 2 cc. active extract of pig's stomach ; 2 cc. water ; 0.1 cc. toluene ; 0.26 cc. ethyl butyrate.  
Increase of acidity 0.8 cc. N/20 KOH ; decomposition 2 per cent.

These experiments certainly show that while a lipolytic enzyme is present in extracts of the mucosa of the stomach, it cannot effect the hydrolysis of fats in the presence of 0.3 per cent hydrochloric acid, and hence any hydrolysis of fats brought about by it in the stomach would probably be confined to the first stages of gastric digestion. The following experiments show further that this enzyme is rendered

permanently inactive by hydrochloric acid of this strength, proving, therefore, that on passing from the stomach into the intestine, the enzyme does not again become active.

*Experiments (Third Series).*

- (1) 2 cc. active extract of pig's stomach ; 2 cc. 0.6 per cent hydrochloric acid ; 0.1 cc. toluene.

This mixture was heated ten minutes at 40°, when 0.2 cc. of litmus solution was added, and the contents of the tube just neutralized with N/20 KOH. 0.26 cc. ethyl butyrate was then added, and the tube again placed in the bath of 40°. The solution remained neutral permanently.

- (2) Repetition of the above gave the same result.

- (3) 2 cc. active extract pig's stomach ; 2 cc. water ; 0.1 cc. toluene.

This mixture was heated for ten minutes at 40°, when 0.2 cc. of litmus solution, 6.8 cc. water,<sup>1</sup> and 0.26 cc. of ethyl butyrate were added. The tube was then again placed in the bath at 40°. The solution became red in five minutes. After heating for twenty-five minutes, it required 0.7 cc. N/20 KOH ; decomposition, 1.76 per cent. When returned to the bath, after neutralization, it became red again almost immediately. These experiments were repeated with extracts made from the stomach of a second animal with like results.

Still another occurrence of lipase, of doubtless great physiological interest, has been found in the small intestine of the pig. A short section of the intestine, including the duodenum and upper part of the jejunum was thoroughly cleansed in running water. At the time the animal was killed a small quantity of fluid was found in the small intestines. After cleansing, the mucosa was scraped off and macerated with coarse white sand and extracted with water. A 10 per cent extract was thus prepared. This extract was quite similar in appearance to the pancreatic extracts. Tubes were prepared containing 4 cc. of water, 0.1 cc. toluene, and 0.26 cc. ethyl

<sup>1</sup> This quantity of water was added in order to make the concentration the same as in Experiment 1.

butyrate. They were then heated in the bath at 40° for five minutes, at the end of which time 1 cc. of the active or boiled extract was added, after which the tubes were heated for fifteen or thirty minutes. The following results were obtained :

	Time in minutes.	cc. N/20 KOH required.	Per cent of hydrolysis.
1	15	0.9	2.26
2	30	1.65	4.14
3 <sup>1</sup>	15	1.00	2.51
4	30	1.30	3.26

The boiled extract showed no activity whatever.

According to these results, the mucous lining of the small intestine possesses a lipolytic activity equal to three-fourths that of the fresh pancreas for equal amounts of tissue. The probable physiological significance of this fact will be briefly discussed in a subsequent part of this paper.

#### *Effect of Filtration.*

In our earlier work with the enzyme, the attempt was made to obtain it in the form of a clear solution, free from all suspended matter of any kind. By repeated filtration we succeeded in obtaining clear solutions, showing only a slight opalescence. Unfortunately, such solutions were always found to be exceedingly weak in lipolytic power. On the other hand, it was found that if the pancreas was thoroughly macerated with sand and the macerated mass thoroughly mixed with water, and simply strained through linen or cotton cloth, an extract of great lipolytic power was obtained. The effect of filtration was invariably to diminish the activity of the solutions. This was proved experimentally for aqueous and glycerin extracts of both the pancreas and liver. The same was also found to hold for the pancreatin of Parke, Davis & Co. A 2 per cent solution of this preparation is yellowish in color and is turbid. In this shape it possesses weak but measurable lipolytic power. On filtering a great many times a clear yellow solution is obtained, which possesses only a trace of its original lipolytic activity. To show the effect of filtration on the liver extract, the following experiments are cited : Before filtering, 1 cc. of a 10 per cent liver extract was found to

<sup>1</sup> In Experiments 3 and 4, 0.1 gram thymol was used as the antiseptic.

hydrolyze 6.28 per cent of ethyl butyrate in fifteen minutes at 40°. After filtering repeatedly through the same filter-paper, it hydrolyzed only 2.76 per cent of ethyl butyrate under the same conditions, showing a falling off in activity of over one-half as the result of filtration.<sup>1</sup> The removal of lipase, along with the suspended matter in the solution, was observed in still another connection. When an active pancreatic extract acts on ethyl butyrate at 40°, the butyric acid produced soon coagulates the proteids in the extract. On filtering, it was found that the clear filtrate possessed little or no lipolytic power, whereas the proteid coagulum was found to be exceedingly active. In view, therefore, of the injurious effect of prolonged filtration, it was deemed advisable to employ extracts which had been prepared in the manner above described, and which had simply been strained through linen or cotton cloth. Care was taken, however, to macerate thoroughly.

#### *Stability of Lipase.*

There seems to be a general impression among those who have worked with this enzyme that in order to obtain active pancreatic extracts they should be prepared within a few hours after the death of the animal.<sup>2</sup> It is true that, as compared with many enzymes, lipase is very unstable. That it does not disappear from the gland, however, as soon as is commonly supposed, is shown by the following experiments: Several pancreases were placed in cold storage, without antiseptic, on July 19, 1900. One cc. of a 10 per cent aqueous extract of a fresh pancreas on July 19, in 4 cc. of water with 0.26 cc. ethyl butyrate and 0.1 cc. toluene in fifteen minutes at 40°, required 2.45 cc. of N/20 KOH for neutralization. It, therefore, hydrolyzed 6.15 per cent of ethyl butyrate. On July 26 one of the pancreases was removed from the cold storage and a 10 per cent aqueous extract was prepared. It had an initial acidity of a 0.2 cc. KOH, and 1 cc. of it hydrolyzed 2.51 per cent of ethyl butyrate under the same condi-

<sup>1</sup> The same thing has been found to hold true in the case of other enzymes. See Vines: *Ann. of Bot.*, 1891, 409; Wortmann: *Bot. Zeit.*, 1890, 37 et seq.; Brown and Morris: *J. Chem. Soc. Trans.* (1893), 604.

<sup>2</sup> Oppenheimer: "Die Fermente," 228, (1900); Shafer: "Text-book of Physiology," Vol. I, p. 339, (1897).

tions as the first. In seven days, therefore, at a temperature of  $4^{\circ}$ , there was a falling off in lipolytic activity of about 60 per cent. Still another pancreas in which putrefactive changes had begun, was observed to possess feeble lipolytic power. Still another preparation of the pig's pancreas throws light on the stability of lipase. The attempt was made to get rid of fat in the pancreatic extract by dissecting the gland as free from fat as possible, then grinding to a stiff paste with dry sand, and drying the resulting mass by exposing it in thin layers on filter-paper for several hours at ordinary temperature in the air. The dried mass was then extracted with ligroin and dried again in the air, and finally a small quantity of thymol was ground into the silicious mass to act as a preservative. An aqueous extract of the sand thus prepared was found to possess lipolytic activity, although it was much less active than the fresh aqueous extract of the pancreas. This preparation was made on July 12th. It was kept in the dark room in a glass-stoppered bottle. On August 17, an aqueous extract of the silicious mass was again made, and this was found to be nearly, if not quite, as active as it was originally. With proper precautions, the extracts of the pancreas and liver can also be preserved for some time without materially losing their activity. That such is the case may be seen from the following:

A 10 per cent aqueous extract of the pancreas was prepared on July 20th. The extract was placed in the refrigerator (temperature  $1^{\circ}$ ), and kept there for several days, its activity being tested at intervals on ethyl butyrate in the following manner: 1 cc. of the enzyme with 4 cc. of water, 0.1 cc. toluene, and 0.26 cc. ethyl butyrate were heated together in a test-tube for fifteen minutes at  $40^{\circ}$ . at the end of which time titration was made with N/20 KOH.

The following results were obtained:

	N/20 KOH required. cc.	Per cent of hydrolysis.
Initial activity of extract	1.63	4.09
Activity of extract after forty-eight hours	1.77	4.44
Activity of extract after seventy-two hours	1.65	4.14

During seventy-two hours, the initial acidity of the extract had increased from 0.1 cc. to 0.25 cc. N/20 KOH. This was allowed for in the above calculations. Similar results have been obtained with the aqueous extracts of the liver of the pig. A 10 per cent aqueous extract was prepared on July 24th and kept on ice for several days in a glass-stoppered bottle. Its activity towards ethyl butyrate was tested at intervals, the experiments being carried out in test-tubes using 1 cc. of the enzyme solution, 4 cc. water, 0.1 cc. toluene, and 0.26 cc. ethyl butyrate. Temperature, 40°; duration of experiments, fifteen minutes.

	N/20 KOH required. cc.	Per cent of hydrolysis.
Initial activity of extract	1.7	4.26
Activity of extract after six hours	2.5	6.27
Activity of extract after forty- eight hours	2.4	6.03

The increase in the activity of these extracts on standing is interesting. The above are by no means the only cases in which such an increase in activity has been observed. The best explanation of this increase in activity on standing would seem to be that during the interval a certain amount of zymogen had been transformed to enzyme. It has also been observed that glycerin extracts of the pancreas are more stable than aqueous extracts of the same activity. Some idea of the stability of the glycerin pancreatic extracts may be gathered from the following observation: A glycerin extract was made on June 15th, 1900, and made use of in the investigation until June 23rd. Some of it was then preserved in sealed tubes in the dark room at summer temperature until August 18th, when it was still found to possess considerable lipolytic activity.

*The Effect of Temperature on the Activity of Lipase.*

It is well known that the activity of lipase is dependent on the temperature. According to Hanriot<sup>1</sup> the optimum temperature of the enzyme is 55°. At 60° he observed it to become considerably slower in its action, and at 72° it was found

<sup>1</sup> Compt. rend., 124, 235 (1894).

to lose its activity altogether. Towards ethyl butyrate the activity of pancreatic lipase has been found to increase more or less regularly from  $0^{\circ}$  to  $40^{\circ}$  C. Above this temperature there is a gradual falling off in activity with rise of temperature. On exposure to a temperature somewhere between  $65^{\circ}$  and  $70^{\circ}$  for five minutes, a 10 per cent pancreatic extract loses its activity altogether. The activity of hepatic lipase varies much more with the temperature between  $0^{\circ}$  and  $40^{\circ}$  C. than that of the pancreatic enzyme as may be seen from the following experiments: Tubes containing 4 cc. of water, 0.1 cc. of toluene, and 1 cc. of a 10 per cent extract of the liver or pancreas were kept in baths at  $40^{\circ}$ ,  $30^{\circ}$ ,  $20^{\circ}$ ,  $10^{\circ}$ ,  $0^{\circ}$ , and  $-10^{\circ}$  C., respectively, for five minutes in order to let them acquire the temperature of the bath. At the end of this time 0.26 cc. of ethyl butyrate was added to each tube, after which the tubes were allowed to remain in their respective baths thirty minutes, when they were placed in ice-water and titrated with N/20 KOH. The following results were obtained:

*With the Pancreatic Extract.*

Temperature.	N/20 KOH required. cc.	Per cent of hydrolysis.
$40^{\circ}$	1.125	2.82
$30^{\circ}$	1.26	3.16
$20^{\circ}$	1.00	2.51
$10^{\circ}$	0.75	1.88
$0^{\circ}$	0.50	1.25

*With the Hepatic Extract.*

Temperature.	N/20 KOH required. cc.	Per cent of hydrolysis.
$40^{\circ}$	4.5	11.29
$30^{\circ}$	2.375	5.96
$20^{\circ}$	2.10	5.27
$10^{\circ}$	1.55	3.89
$0^{\circ}$	0.9	2.26
$-10^{\circ}$	0.28	0.70

Similar results have been obtained by Hanriot<sup>1</sup> for serum and pancreatic lipase. He found the latter, for example, to exhibit the same activity between  $15^{\circ}$  C. and  $42^{\circ}$  C., whereas

<sup>1</sup> Compt. rend., 124, 778 (1897).

the serum lipase hydrolyzed twice as much monobutyrim at 42° C. as at 15° C. In this connection it is well to bear in mind that Schmiedeberg<sup>1</sup> seems to have made a distinction between the enzyme of the liver which splits hippuric acid, fats, etc, and which he calls histozyme, and ordinary pancreatic lipase. On the other hand, Nencki<sup>2</sup> has shown that the pancreas can also split hippuric acid.

*On the Relative Stability of Different Ethereal Salts towards Lipase.*

It is well known that other ethereal salts besides the fats are hydrolyzed in the intestine. Baas,<sup>3</sup> for example, found that, in the dog, salol was hydrolyzed in one case to the extent of 69 per cent and in another to 43.95 per cent. Methyl salicylate to 24.75 per cent and ethyl salicylate to 21.20 per cent. Heritsch<sup>4</sup> has also found that lipase could hydrolyze ethereal salts, for example, ethyl acetate. It occurred to us, therefore, that it would be interesting to measure the hydrolysis of a few of the commoner ethereal salts. Unfortunately, at this particular time only a limited number of these were on hand of sufficient purity for the purposes of the investigation. Ethyl formate, ethyl acetate, ethyl propionate, and ethyl butyrate were therefore selected for the experiments. Tubes were prepared containing 4 cc. of water, 0.1 cc. toluene, and 1 cc. 10 per cent pancreas extract. These were heated in the bath at 40° C. for five minutes. The ethereal salt to be tested was then added in the proportion of twice the molecular weight of the salt in milligrams. The tubes were then heated for fifteen minutes, when they were placed in ice-water and titrated with N/20 KOH. The following results were obtained :

	Quantity of ethereal salt used. Gram.	N/20 KOH required. cc.	Per cent of hydrolysis.
Ethyl formate	0.148	0.65	1.60
“ acetate	0.176 <sub>7</sub>	0.37	0.93
“ propionate	0.204	0.42	1.05
“ butyrate	0.232	1.26	3.13

<sup>1</sup> Arch. f. Exp. Path. u. Pharm., 14, 379 (1881).

<sup>2</sup> Arch. f. Exp. Path. u. Pharm., 20, 367 (1886).

<sup>3</sup> Ztschr. f. physiol. Chem., 14, 416 (1890).

<sup>4</sup> Centrbl. Med. Wis., 1875, 449.



A second series of experiments, exactly like the above, was tried, a more active pancreatic extract being used. The following results were obtained :

	N/20 KOH required. cc.	Per cent of hydrolysis.
Ethyl formate	0.7	1.75
“ acetate	0.7	1.75
“ propionate	1.15	2.87
“ butyrate	1.75	4.37

Both series exhibit the same order of stability and both show that the higher the molecular weight of the acid, the more readily is its ethyl ester hydrolyzed by lipase. Ethyl formate is very easily hydrolyzed by pure water. This would probably account for the high values obtained with this compound.

In this connection it occurred to us that it might prove interesting, and perhaps valuable for future work upon this subject, to compare quantitatively the hydrolyzing power of certain acids with that of lipase upon ethyl acetate and ethyl butyrate. Hence, normal solutions of hydrochloric, acetic, and butyric acids were made use of in very much the same way as the enzyme in the experiments described in the above. Tubes were prepared containing 4 cc. of water and 0.176 gram of ethyl acetate. These were then heated in the bath at 40° C. for five minutes. One cc. of the normal acid was then run in and the tube heated for the desired length of time, at the end of which it was titrated with N/20 KOH. The following are the results obtained :

Acid.	Time. Minutes.	N/20 KOH required. cc.	Per cent of hydrolysis.
Water	15	0.05	0.13
	60	0.00	0.00
Hydrochloric	15	2.45	6.14
	30	4.45	11.15
Acetic	15	0.05	0.13
	60	0.4	1.0
Butyric	15	none	none
	60	“	“

*Second Series with N-Hydrochloric Acid.*

Time. Minutes.	N/20 KOH required. cc.	Per cent of hydrolysis.
15	2.45	6.14
30	4.45	11.15
45	6.10	15.29
60	8.15	20.43
90	10.75	26.95
120	14.05	35.21

Similar experiments on the hydrolysis of ethyl butyrate by acids gave the following results :

Conditions of experiment: Temperature, 40° C. ; quantity of ethyl butyrate used in each experiment = 0.232 gram.

Acid.	Time. Minutes.	N/20 KOH required. cc.	Per cent of hydrolysis.
Hydrochloric	30	0.05	0.12
	60	0.8	2.00
	90	1.3	3.25
	120	1.5	3.75
Acetic	30	none	none
	60	0.1	0.25
	90	0.1	0.25
	120	0.3	0.75

Several interesting conclusions may be drawn from these results, the chief of which is the remarkable difference displayed by lipase and hydrochloric acid in effecting the hydrolysis of ethyl acetate and butyrate. Both pancreatic and hepatic lipase hydrolyze ethyl butyrate considerably more rapidly than the acetate, and this notwithstanding the fact that the latter is entirely in solution under the condition of the experiment, whereas the former is not. On the other hand, normal hydrochloric acid hydrolyzes the acetate about ten times as rapidly as the butyrate. As regards the cause of this remarkable difference between these two processes we are at present in the dark. It certainly offers an interesting field for further investigation.

*On the Effect of Antiseptics on Lipase.*

For certain parts of the work it was necessary to exercise considerable care in the choice of an antiseptic. It was,

therefore, thought desirable to study the effect of a number of the commoner antiseptics on this enzyme. Such a study seemed all the more desirable inasmuch as but few, if any, systematic studies of the action of antiseptics in general on enzymes have been undertaken. Some observers have studied the effect of one particular substance, and others that produced by another, but few, if any, general comparisons of the action of antiseptics have ever been made. The first series of experiments was made with salicylic acid. Tubes were prepared containing water (quantity indicated in the following table), 0.1 cc. of toluene, 1 cc. of 20 per cent pancreas extract, together with a certain amount of salicylic acid, varying in the amount from 0.1 to 1 cc. of a 0.5 per cent solution. The tubes were heated for five minutes at 40° C., when 0.26 cc. of ethyl butyrate was added. The tubes were then allowed to remain in the bath at 40° for fifteen minutes, when they were removed and titrated with N/20 KOH.

Quantity of water used. cc.	Quantity of 0.5 per cent solution salicylic acid used. cc.	N/20 KOH required. cc.	Per cent of hydrolysis.
4.0	none	2.25	5.65
3.9	0.1	2.12	5.32
3.5	0.5	1.4	3.51
3.0	1.00	0.2	0.50

This series exhibits a regular decrease in the activity of the enzyme in the presence of increasing amounts of salicylic acid.<sup>1</sup>

In the second series of experiments the following substances were employed in solution in the proportion of 1 to 1000: Silver nitrate, mercuric chloride, hydrocyanic acid, salicylic acid, thymol, and sodium fluoride. Tubes were prepared containing 4 cc. of water or of the solution of the antiseptic to be tested and 1 cc. of the enzyme (15 per cent pancreatic extract). The tubes were then heated for five minutes at 40°, at the end of which time 0.26 cc. of ethyl butyrate was added to each tube. The tubes were then allowed to remain in the bath at 40° for fifteen minutes, at the end of which time they

<sup>1</sup> An investigation of the power of salicylic acid to prevent the fermentation of wine must by Neubauer gave similar results. See *J. prakt. Chem.* (2), 11, 1.

were titrated with N/20 KOH. The following are the results :

Substance used.	N/20 KOH required. cc.	Per cent of hydrolysis.
Water	1.8	4.52
Hydrocyanic acid	1.7	4.27
Thymol	1.6	4.02
Mercuric chloride	0.3	0.75
Silver nitrate	0.15	0.38
Salicylic acid	none	none
Sodium fluoride	"	"

In the third series of experiments, the following substances were tried : Potassium cyanide, ammonium oxalate, and toluene. These substances were used in a solution containing 1 : 1000. Tubes were prepared containing 4 cc. of water, or of the solution of the antiseptic to be tested, and 1 cc. of pancreatic extract. These were heated at 40° for five minutes, when 0.26 cc. of ethyl butyrate was added to each tube. They were allowed to remain in the bath at 40° C. for fifteen minutes and then they were titrated with N/20 KOH. The following are the results :

Substance used.	N/20 KOH required. cc.	Per cent of hydrolysis.
Water	1.4	3.51
Ammonium oxalate	1.25	3.14
Toluene	1.15	2.89
Potassium cyanide	0.3	0.75

The effect of antiseptics 1 : 1000 was next tried on a 10 per cent hepatic extract, which had been made up originally without an antiseptic. Ethyl acetate was employed in this series of experiments. Tubes were prepared containing 3 cc. of water, 1 cc. of enzyme, and 1 cc. of the antiseptic. These tubes were then heated at 40° for fifteen minutes, after which 0.19 cc. ethyl acetate was added. The tubes were then allowed to remain in the bath at 40° for thirty minutes, when they were titrated with N/20 KOH. The following are the results :

Substance used.	N/20 KOH required. cc.	Per cent of hydrolysis.
Water	2.65	6.62
Toluene	2.90	7.25
Chloroform	2.50	6.25
Hydrocyanic acid	2.30	5.75
Mercuric chloride	2.00	5.00
Thymol	1.85	4.63
Silver nitrate	1.60	4.00
Salicylic acid	1.50	3.75
Osmic acid	1.45	3.63
Sodium fluoride	0.10	0.25

After titration the tubes were allowed to stand at ordinary temperature, 30° C., for an hour and a half, when they were titrated a second time, with the following results :

Substance used.	N/20 KOH required. cc.	Per cent of hydrolysis.
Water	3.02	7.55
Toluene	3.90	9.75
Chloroform	3.65	8.82
Hydrocyanic acid	3.40	8.50
Mercuric chloride	2.70	6.75
Thymol	3.00	7.50
Silver nitrate	2.20	5.50
Salicylic acid	3.05	7.60
Osmic acid	2.45	6.12
Sodium fluoride	0.20	0.50

Finally, the attempt was made to determine the effect of a number of antiseptics on liver and pancreatic extracts of about the same activity towards ethyl butyrate. Therefore, a 10 per cent liver extract was compared with a 20 per cent pancreatic extract under the following conditions : Tubes were prepared containing 3 cc. of water, 1 cc. of the antiseptic (1 : 1000) and 1 cc. of the enzyme. These were heated at 40° C. for five minutes to give the antiseptic a chance to act. Then 0.26 cc. ethyl butyrate was added and the tubes allowed to remain in the bath at 40° C. for fifteen minutes, when they were removed and titrated with N/20 KOH. The following are the results :

*Series with 10 Per Cent Liver Extract.*

Substance used.	N/20 KOH required. cc.	Per cent of hydrolysis.
Water	3.4	8.54
Formic aldehyde	3.7	9.29
Iodoform	3.5	8.78
Cocaine hydrochloride	3.5	8.78
Strychnine sulphate	3.45	8.66
Phenol	3.45	8.66
Toluene	3.3	8.28
Chloroform	3.25	8.16
Mercuric chloride	3.2	8.03
Bromoform	2.9	7.28
Thymol	2.9	7.28
Hydrocyanic acid	2.75	6.90
Salicylic acid	2.60	6.53
Silver nitrate	2.55	6.40
Osmic acid	2.00	5.02
Sodium fluoride	0.45	1.13
Hydrochloric acid	0.25	0.63
Hydrofluoric acid	0.25	0.63

*Series with 20 Per Cent Pancreatic Extract.*

Substance used.	N/20 KOH required. cc.	Per cent of hydrolysis.
Water	2.65	6.75
Bromoform	2.75	6.90
Chloroform	2.65	6.75
Hydrogen peroxide	2.50	6.27
Formic aldehyde	2.40	6.02
Salicylic acid	2.40	6.02
Thymol	2.30	5.77
Hydrocyanic acid	2.20	5.52
Iodoform	2.15	5.40
Mercuric chloride	2.15	5.40
Osmic acid	1.95	4.89
Strychnine sulphate	1.90	4.77
Toluene	1.80	4.52
Phenol	1.65	4.14
Silver nitrate	1.60	4.02
Hydrofluoric acid	0.50	1.25
Hydrochloric acid	0.40	1.00
Sodium fluoride	0.30	0.75

It is believed that in the last two series of experiments a mistake was made in not allowing the antiseptic to remain in

contact with the enzyme for a greater length of time in order that the effect of the weaker of them might have been more pronounced.

It will be observed that certain of the antiseptics tested exert the same effect on both the pancreatic and liver extracts; for example, chloroform is almost without effect, and thymol, hydrocyanic acid, and sodium fluoride each reduces the activity of the two extracts to the same extent. On the other hand, some of the substances used behave differently towards the two enzymes. For example, while strychnine sulphate and phenol both reduced the activity of the pancreatic extract about 30 per cent, they were without effect on the activity of the liver extract. On the other hand, osmic and salicylic acids seem to exert a more detrimental effect on the hepatic than on the pancreatic lipase. While perhaps not conclusive, these results are suggestive at least, for, if after repeated trials, it were to turn out that several substances exerted a different effect upon liver and pancreatic lipase, it would probably indicate that the two enzymes are in reality different substances. Upon pancreatic lipase especially, nearly all kinds of substances seem to exert a harmful effect. Towards a number of them, on the other hand, the lipase of the liver is more stable. Generally speaking, the more germicidal and antiseptic the substance, the greater its power to inhibit and destroy the activity of lipase. Substances like silver nitrate, mercuric chloride, salicylic acid, and osmic acid exert a more pronounced detrimental effect than the weaker antiseptic substances—such as toluene, chloroform, thymol, etc. One point of especial interest in this connection is the remarkably destructive action of sodium fluoride on lipase. In all of our tests this substance has been found to exert the most destructive influence upon lipase of any substance yet tried, unless it is hydrofluoric acid itself. The effect of acids in general has also been found to be very injurious.<sup>1</sup>

<sup>1</sup> Quite recently, in fact since this article was written, Kastle and Hardin have been engaged in studying the toxic action of different acids on lipase. It is their intention to present the results obtained in the form of a separate communication. It may not be out of place to state in this connection, however, that it has been found in general, that the toxic effect of acids upon lipase is proportional to their strength.

*On the Effect of Concentration of the Enzyme on the Velocity of the Reaction.*

The attempt has been made to determine the effect of concentration on the activity of hepatic and pancreatic lipase. According to some observers, the rate of hydrolysis by lipase is proportional to the concentration of the enzyme, especially if the conditions are those most favorable to the reaction. In order to determine the effect of concentration of the enzyme on its activity, concentrated extracts, usually 50 per cent, of the pancreas and liver were prepared, and from these the more dilute extracts, such as 5, 10, 20, and 40 per cent, respectively, were made by dilution. Tubes were then prepared containing 4 cc. of water, 0.1 cc. of toluene, and 0.19 cc. of ethyl acetate. The tubes were heated for five minutes at 40° C., at the end of which time 1 cc. of the enzyme of a given concentration was then added, after which the tubes were heated for thirty minutes. They were then removed from the bath and titrated with N/20 KOH. The following results were obtained :

Concentration of the pancreatic extract. Per cent.	N/20 KOH required. cc.	Per cent of hydrolysis.
5	0.13	0.33
10	0.25	0.625
20	1.08	2.70
40	2.00	5.00
Concentration of the hepatic extract. Per cent.	N/20 KOH required. cc.	Per cent of hydrolysis.
5	0.8	2.00
10	1.35	3.37
20	3.88	9.70
40	6.90	17.25

Still another series, with an extract which was prepared from the pig's liver, that had stood for twenty-four hours on ice, gave the following results :



Conditions of the experiments the same as in the first two series.

Concentration of the hepatic extract. Per cent.	N/20 KOH required. cc.	Per cent of hydrolysis.
5	1.2	3.00
10	2.02	5.05
20	2.93	7.32
40	4.50	11.25

These results leave no room for doubt that the rate of change increases with the quantity of enzyme present in the solution, in fact in one of the above series, *viz.*, that of the liver extract it is approximately proportional to the concentration of the enzyme. The fact, however, must be borne in mind in the interpretation of the above results, that the fatty acid produced in the hydrolysis of the ethereal salt soon coagulates the proteid present in the solution, and, as has already been pointed out, this coagulation removes the lipase more or less completely from solution; and while the coagulum still possesses considerable lipolytic power, it is doubtful if the enzyme acts to as great advantage as when in solution. We have not yet had the opportunity of comparing the activity of the coagulum with that of the original extract. It is a factor, however, which might very materially vitiate the results and should certainly be taken into consideration.

*On the Effect of the Concentration of the Ethereal Salt on the Velocity of the Reaction.*

The hydrolysis of an ethereal salt by lipase certainly presents some analogy at least to the hydrolysis of such a compound by an acid. On account of the instability of the lipase itself, however, its action rather resembles that of the hydrolysis of an ethereal salt by an acid itself so unstable as to be constantly undergoing a gradual decomposition during the change. The question therefore suggests itself in this connection, Is the amount of hydrolysis for any given interval, proportional to the active mass of the ethereal salt? Hanriot and Camus<sup>1</sup> have observed that the rate of hydrolysis varies

<sup>1</sup> Compt. rend., 124, 235 (1897).

slightly with the quantity of ethereal salt present. In order to test this point further the equation for a reaction of the first order  $\frac{1}{\theta} \log \frac{A}{A-x} = k$  was applied to the reaction in hand.

Tubes containing 4 cc. of water, 0.1 cc. toluene, and 0.26 cc. ethyl butyrate were prepared and heated for five minutes at 40° C. One cc. of a 10 per cent extract was then added and the tubes heated for the desired length of time and titrated with N/20 KOH. The following results were obtained :

Time. Minutes.	N/20 KOH required. cc.	Per cent of hydrolysis.	k.
5	2.60	6.53	0.01354
10	3.45	8.66	0.00907
15	3.40	8.53	0.00592
20	3.80	9.54	0.00500
25	4.25	10.67	0.00500
30	3.75	9.41	0.00329
60	6.90	17.32	0.00316
120	10.10	25.35	0.00244
180	11.3	28.36	0.00184

*One Minute Series.*—Conditions the same as in the preceding.

Time. Minutes.	N/20 KOH required. cc.	Per cent of hydrolysis.	k.
1	1.3	3.26	0.03344
2	1.8	4.52	0.02296
3	1.95	4.89	0.01657
4	2.30	5.77	0.01481
5	2.60	6.53	0.01354

The following series was tried to show the effect of varying the amount of ethyl butyrate. The tubes contained 4 cc. of water, 0.1 cc. toluene, and 1 cc. of the 10 per cent liver extract used in the preceding series. The tubes were heated at 40° C. for five minutes, at the end of which time a certain quantity of ethyl butyrate was added and the tubes heated for five minutes at 40° C., and then titrated. The following results were obtained :

Quantity of ethyl butyrate employed.		N/20 KOH required.	Quantity of ethyl butyrate hydrolyzed.	
cc.	Gram.		cc.	Gram.
0.065	= 0.0575	2.1		0.0122
0.13	= 0.1150	2.7		0.0156
0.195	= 0.1725	2.6		0.0151
0.26	= 0.2300	3.2		0.0185

According to these results, the actual amount of ethyl butyrate hydrolyzed by the enzyme in a given time, is very largely independent of the concentration of the ethereal salt. It was thought possible that the fact, that in all of these experiments a certain amount of the butyrate remained undissolved, might offer an explanation of these results. It was thought desirable, therefore, to repeat some of the work on the concentration of the ethereal salt, using ethyl acetate in the place of ethyl butyrate, for the reason that the former is quite soluble in water. A solution of ethyl acetate was prepared containing 0.01414 gram of the compound per cubic centimeter. Forty cc. of this solution was placed in a glass-stoppered flask, together with 0.5 cc. toluene, and heated in the bath at 40° C. until it had reached the temperature of the bath. Ten cc. of 10 per cent liver extract, which had also been warmed to the temperature of the bath, were then added, and the time of the experiments was reckoned from this instant. The flask was constantly shaken, and at certain intervals 5 cc. of the mixture were withdrawn from the flask by means of a pipette and titrated with N/20 KOH. The results are given below :

Time. Minutes.	N/20 KOH required. cc.	Per cent of hydrolysis.	k.
5	0.45	3.50	0.00714
10	0.75	5.83	0.00603
15	0.90	6.99	0.00484
20	1.00	7.77	0.00404
30	1.30	10.10	0.00355
45 $\frac{1}{4}$	1.65	12.82	0.00303
60	1.85	14.37	0.00258

The effect of varying the concentration of the ethyl acetate was tried in the following manner : Ten per cent extract of liver used. Temperature, 40° C. Time, fifteen minutes.

Substance used in experiment.	N/20 KOH required. cc.	Quantity of ethyl acetate originally present. Gram.	Quantity of ethyl acetate hydrolyzed. Gram.
4 cc. ethyl acetate solution and 1 cc. of enzyme	0.9	0.05656	0.003952
3 cc. ethyl acetate solution, 1 cc. water, and 1 cc. enzyme	0.875	0.04242	0.003861
2 cc. ethyl acetate solution, 2 cc. water, and 1 cc. enzyme	0.9	0.02828	0.003952
1 cc. ethyl acetate solution, 3 cc. water, and 1 cc. enzyme	0.775	0.01414	0.003403

It will be observed that, as in the case of ethyl butyrate, the hydrolysis of ethyl acetate by lipase is largely independent of the concentration of the ethereal salt.

In this connection the attempt has also been made to determine whether the hydrolysis of ethyl butyrate by lipase is complete. With this in view, two bottles were prepared as follows :

No. 1 contained 40 cc. of water, 10 cc. of 10 per cent pancreatic extract, 1 cc. toluene, 0.65 cc. ethyl butyrate.

No. 2 contained 40 cc. of water, 10 cc. of 10 per cent hepatic extract, 1 cc. toluene, 0.65 cc. ethyl butyrate.

These were allowed to stand at ordinary temperature for several days. At intervals during this time, 5 cc. of the contents were withdrawn by means of a pipette and titrated with N/20 KOH. The following results were obtained :

	Time. Hours.	N/20 KOH required. cc.	Per cent of hydrolysis.
5 cc. No. 1 (pancreatic) lipase	19	3.5	35.0
5 " " " "	19	3.5	35.0
5 " " " "	47	4.3	43.0
5 " " " "	47	4.15	41.5

	Time. Hours.	N/20 KOH required. cc.	Per cent of hydrolysis.
5 cc. No. 1 (pancreatic) lipase	137	4.3	43.0
5 " " "	137	4.3	43.0
5 " No. 2 (hepatic)	19	7.1	71.0
5 " " "	19	7.25	72.5
5 " " "	47	9.35	93.5
5 " " "	47	9.55	95.5
5 " " "	47	9.4	94.0
5 " " "	137	9.2	92.0

After titration these tubes were allowed to stand for a time. In every case the contents of the tube became acid in reaction, thereby indicating that active enzyme was still present in the solution. The above results are such as to indicate that except when relatively large amounts of the enzyme are employed, the reaction is incomplete. Whether with lipase of different origin or with varying amounts of the same enzyme the limit reached in all cases would be the same is a matter which can only be settled by further investigation. The fact that the hydrolysis is not complete under ordinary circumstances is in keeping with the more or less regular falling off in the velocity of the reaction described in the above, and is probably to be explained by the fact that the hydrolysis of an ethereal salt by lipase is a reversible process, and that the enzyme, as a catalytic agent, is concerned chiefly in bringing about a condition of chemical equilibrium between the ethereal salt and water and the products of the hydrolysis. Acids also have been found to greatly inhibit the activity of the enzyme, so that the great falling off in the rate of hydrolysis is doubtless, to some extent at least, assignable to this cause.

#### *The Reversibility of the Action of Lipase.*

In spite of the vast amount of work which has been done upon the enzymes, we possess at present no unifying conception as to the manner of their action. For the solution of this problem, we must probably look to the study of the kinetics of enzyme action, and one of the first questions to present itself

in this connection is, Are the enzymes reversible in their action? If so, then an accumulation of the products of their action should have an increasingly inhibiting effect on the further progress of the change, until finally equilibrium would be established between the initial substance and the products of the change.

O'Sullivan and Thompson,<sup>1</sup> in their exhaustive study of the action of invertase on cane-sugar, could not observe any inhibiting effect from the presence of the products of the change. On the other hand, Sheridan Lea<sup>2</sup> found the digestion of starch by salivary diastase to be more rapid and much more complete when the products of the digestion were removed by dialysis than when the digestion was performed under identical conditions, but without this precaution. He obtained similar results in his investigation of tryptic digestion. As to the effect of peptone on peptic digestion, the views are somewhat contradictory. Kühne<sup>3</sup> states that peptone has a retarding effect on peptic digestion, while the opinion of Chittenden and Ely<sup>4</sup> contradicts this. Tamman,<sup>5</sup> from his studies of this phase of the problem, arrived at the following conclusions:

1. Hydrolyses produced by enzymes are incomplete, especially if the quantity of material acted on is large (invertase and rennin are exceptions to this).
2. The incompleteness of the action is due to the accumulation of the products of the fermentation.
3. Removal or dilution of these products, or elevation of the temperature, allows the fermentation to continue.

It would appear that the results obtained by Tamman are easily explicable on the supposition that the enzymes are reversible in their action, the reaction ceasing when the products of the hydrolysis reach a definite concentration in consequence of equilibrium being established. As Tamman failed to get any indication experimentally that the enzymes are capable of effecting the synthesis of the substances they are

<sup>1</sup> J. Chem. Soc., **57**, 926 (1890).

<sup>2</sup> Jour. of Physiology, **11**, 226 (1890).

<sup>3</sup> Lehrbuch d. Phys. Chemie, 1866, S. 39.

<sup>4</sup> Jour. of Physiology, **3**, 327.

<sup>5</sup> Ztschr. physiol. Chem., **16**, 271 (1892); Ztschr. physikal. Chem., **28**, 426 (1895).

capable of hydrolyzing, he was forced to explain his results in another way. He advanced the view that the products of the hydrolysis act on the enzyme, transforming it into an inactive modification, and that on removal of these products it is converted into the active modification again.

Oppenheimer,<sup>1</sup> accepting Tamman's results as final, sought to supply a unifying conception of the action of enzymes. He believes the enzymes are capable of inducing only exothermic reactions—that they are only capable of setting free potential energy, and that none of the endothermic, that is, synthetic processes taking place within the organism, can be classed as enzymic, but must be attributed to the peculiar activity of living protoplasm.<sup>2</sup> He admits, however, that this view is completely at variance with the recent work of Hill,<sup>3</sup> who has proved that the action of maltase on maltose is reversible,—first, by showing that maltase can effect the synthesis of maltose from glucose, and, secondly, by showing that the action of maltase on maltose tends to an equilibrium, which is the same whether we start with glucose or an equivalent quantity of maltose.

It is believed that the results reached in this investigation of lipase throw still further light on the subject and greatly strengthen the belief that all enzyme action would probably prove to be reversible if proper conditions of concentration, etc., could be attained.

In many instances, however, it will probably not be practicable to secure the proper conditions, for as in the rennin coagulation of caseinogen solutions, one of the products of cleavage seems to undergo instantaneous rearrangement in the presence of soluble calcium salts, and is thereby removed from the field of activity, thus rendering reversibility impossible. Then again, in some cases, for example, the action of invertase on cane-sugar, the reaction seems to be so nearly complete in one direction that it is doubtful whether reversibility could be demonstrated experimentally. While the catalysis of ethers by strong acids is practically complete, still these are typical reversible reactions. In attempting to determine whether lipase is reversible in its action, it was decided to test its power to ef-

<sup>1</sup> "Die Fermente und ihre Wirkungen," Leipzig, 1900, S. 55.

<sup>2</sup> The same view has been expressed by Nasse. *Maly's Jahrsbr.*, 1894, S. 718.

<sup>3</sup> *J. Chem. Soc.*, 73, 634 (1898).

fect the synthesis of ethyl butyrate, inasmuch as this substance possesses the following advantages over a true fat: First, it possesses such a characteristic odor that this alone serves as a very delicate and unmistakable test for its presence. Secondly, in order to effect the synthesis of a fat, it would be necessary, or at least highly desirable, to have the extract of the enzyme free from fat. Up to this time we have not been able to prepare a pancreatic extract free from fat without greatly diminishing its lipolytic power. In the synthesis of ethyl butyrate, however, it would not be necessary to remove the fat, and hence it would be possible to employ the most active pancreatic extract obtainable. Finally, a demonstration of the power of lipase to effect the synthesis of ethyl butyrate would be as conclusive as the synthesis of a fat for the reason that the compounds are exactly analogous from a chemical point of view.

*Experiment 1.*—5 cc. N/100 butyric acid, 2 cc. of 13 per cent alcohol, and 1 cc. of diluted glycerin extract of pig pancreas were sealed in a test-tube, and heated at  $48^{\circ}.5$  for thirty-six hours. When opened it had distinctly the odor of ethyl butyrate.

*Experiment 2.*—A mixture of 180 cc. of N/40 butyric acid, and 72 cc. of 30 per cent alcohol was divided into two equal parts. To part 1, 25 cc. of a 10 per cent glycerin extract of pig pancreas was added; 25 cc. of the same glycerin extract which had been brought to boiling, and then cooled, was added to part 2. The flasks were left open at ordinary temperature. In a few minutes the flask containing the fresh enzyme had developed a decided odor of ethyl butyrate. The flask was then corked and allowed to stand a week when the odor of ethyl butyrate was still perceptible. The flask containing the boiled enzyme was also corked and was allowed to stand a week under the same conditions. At no time could the odor of ethyl butyrate be detected in the control experiment. Exactly similar experiments were carried out in the presence of toluene water with similar results. Two flasks were also made up, each containing 0.25 gram of  $\beta$ -naphthol. Here, also, the odor of ethyl butyrate was



apparent in the flask containing the active enzyme, while in the flask containing the boiled enzyme there was never the faintest odor of the ethereal salt. Similar results were obtained with glycerin extracts of the cow pancreas. In these experiments, the only test for the production of the ethereal salt was the odor, and although this is very delicate and unmistakable, it seemed desirable to obtain, if possible, larger quantities of the substance. With this in view, the following experiment was made :

Four hundred grams of pig pancreas (which had been removed from the animal one and a half hours) was thoroughly ground up with sand and extracted with water, the extract being made up to 2000 cc. This was divided into two parts of 1000 cc. each. One part was placed in a balloon flask (A) of 4 liters capacity, while the other part was boiled for three minutes. After cooling, enough water was added to supply that lost in boiling. It was then placed in a flask (B) similar to (A). To each of these flasks 2 grams of powdered thymol were added as antiseptic. Each of the flasks was provided with a three-hole rubber stopper, through which passed : 1. A separating funnel ; 2. A tube reaching to the bottom of the flask with a small aperture at the end and connected with an apparatus for giving a current of air ; and 3. A tube connecting the flask with a condenser. A distilling bulb, with its delivery tube drawn out to a capillary opening, and packed in ice, was used as a receiver. The inner tube of the condenser extended to the bottom of the receiver, and the connection between receiver and condenser was made tight with rubber tubing. 3800 cc. of practically N/10 butyric acid (5 cc. = 9.2 cc. N/20 KOH) was made up. This was divided into two equal parts, and to each part was added 100 cc. of 95 per cent alcohol and 4 grams of powdered thymol. One part of this mixture was added to flask (A) and the other simultaneously to flask (B). It was allowed to flow into the flasks very slowly through the separating funnels, four and a half hours being consumed in the operation. The flasks were kept in water-baths at laboratory temperature, 23° to 27°, and both under identical conditions, with respect to sunlight, etc. The initial acidity of the boiled and unboiled extract was the same,

*viz.*, 1 cc. = 0.3 cc. N/20 KOH. The initial activity of the enzyme was taken, and found to be high. In a tube containing 4 cc. of water, 1 cc. of extract, 0.26 cc. ethyl butyrate, and 0.1 cc. toluene, and heated at 40° C. for fifteen minutes, 6.45 per cent of the ethyl butyrate was hydrolyzed. The flasks were allowed to stand forty hours with occasional shaking, both flasks being shaken equally. In order to separate any ethyl butyrate, which might have been produced, the flasks were then heated on the water-bath, the distillation being carried on in a slow current of air. About 25 cc. of the distillate were collected in each case.<sup>1</sup> The odor of the distillate from flask (A) indicated plainly and unmistakably the presence of ethyl butyrate; it also contained some alcohol and butyric acid, but the odor of these could not be detected on account of the butyric ether. In the distillate from the blank (B), the presence of even a trace of the ether was considered very doubtful by all who examined it, while the odor of alcohol and butyric acid were distinct. The distillate obtained from (A) was redistilled from a water-bath (this time no current of air was used), and 5 cc. of a clear distillate was collected. This was still faintly acid with butyric acid and contained some alcohol.

A small portion of this distillate was reserved for experiment and the remainder was poured into water. The mixture at once became turbid and a light ethereal oil rose to the surface. Altogether about 1 cc. of impure ethyl butyrate was obtained in this experiment. Hence about 5 per cent of the butyric acid present had been transformed into the ethereal salt. This quantity was too small for purification and hence no analysis of it was attempted. Its characteristic odor, however, together with its other properties, and its mode of formation left no room for doubt regarding its composition. A small amount of it was saponified with caustic soda, and the solution evaporated to dryness. On adding sulphuric acid to the residue the odor of butyric acid was perceptible at once.

<sup>1</sup> Previous experiment had shown that on distilling a mixture of ethyl butyrate and a large amount of water, practically all the ethereal salt passes over in the first portions of the distillate.

The first distillate from flask (B), *viz.*, that obtained in the control experiment, was treated in exactly the same manner as that from flask (A), *i. e.* the first distillate was distilled a second time and the first 5 cc. of distillate, No. 2, collected. This second distillate had only a trace of the odor of ethyl butyrate, and when poured into water it dissolved without turbidity and no ethereal oil separated on standing. The conduct of the second distillate from (A) and (B) towards lipase was also tested. Tubes were prepared containing 4 cc. of water, 1 cc. of enzyme, 0.1 cc. toluene, and 0.26 cc. of the second distillate from (A) or (B).

The following results were obtained :

With hepatic extract ; time, 15 minutes ; temperature, 40° C.

	N/20 KOH required. cc.
(1) 2nd distillate (A)	0.65
(2) " " (A)	0.70
(1) " " (B)	none
(2) " " (B)	0.05

With pancreatic extract ; time, 50 minutes ; temperature, 40° C.

	N/20 KOH required. cc.
(1) 2nd distillate (A)	0.65
(2) " " (B)	none

Control experiments on the second distillate from (A) using the boiled enzyme, showed no hydrolysis even after long standing. These results prove the presence of an ethereal salt in the second distillate from (A), but none, or at best only traces thereof, in the second distillate from (B).

From these experiments it would seem that lipase is reversible in its action upon ethyl butyrate at least.

The fact that lipase is reversible in its action will doubtless afford an explanation of a number of somewhat obscure physiological processes. For example, Schmiedeberg<sup>1</sup> has shown that the kidney of the pig is capable of splitting hippuric acid into benzoic acid and glyocol, and that it is also capable of effecting the synthesis of hippuric acid from these substances.

<sup>1</sup> Arch. f. Exp. Path. and Pharm., 14, 379 (1881).

He attributes the splitting of the hippuric acid to a soluble enzyme which he calls histozyme, and which he succeeded in extracting from this organ, and also from the liver. On the other hand, he believes the synthesis of the hippuric acid to be due to the absence of histozyme, and to be induced by some other agency. According to him, the processes of decomposition and synthesis going on in the living organism, are brought about by entirely different agencies. The formation of hippuric acid being a reversible reaction, however, it would seem more probable that the histozyme simply has the power to hasten the establishment of the equilibrium between benzoic acid and glycocoll. According to this view, if benzoic acid and glycocoll are passed through the kidneys, a certain quantity of hippuric acid would be built up under the influence of the histozyme, whereas if hippuric acid itself were passed through this organ a certain quantity of it would be hydrolyzed by the histozyme. The fact that lipase can effect the synthesis of an ethereal salt, like ethyl butyrate, will doubtless throw some light on two exceedingly interesting and important physiological processes, *viz.*, the absorption of fats and the ripening of fruits. Without entering minutely into the physiological aspects of fat-absorption, it may be observed in passing that serious objections have been urged against the various theories which have been put forward from time to time to account for the absorption of fats in the intestinal tract. It has been pointed out by Rachford<sup>1</sup> that the pancreatic juice is capable of hydrolyzing all the fat of a fatty meal in the period of pancreatic digestion. In the living intestine, therefore, the hydrolysis should be complete, inasmuch as the removal of the products of the hydrolysis by absorption prevents the establishment of equilibrium. On the other hand, the products of the hydrolysis in their transition through the epithelial cells come in contact with a lipolytic enzyme, the presence of which in these cells has been demonstrated in the above (see p. 493). The lipase now finds itself in contact with only fatty acid and glycerin, and hence in acting catalytically to bring about the chemical equilibrium, it effects the synthesis of a fat. This would offer a satisfactory explanation of the presence of fat

<sup>1</sup> Jour. Physiology, 12, 92 (1891).

granules in these cells. As the fatty acid and glycerin diffuse out of these cells through the basement membrane, the fat in these cells would speedily disappear were it not that these substances were constantly being absorbed from the lumen of the intestine. When absorption ceases, however, the fat present in the epithelial cells is at once hydrolyzed by the lipase present. This hydrolysis is in all probability complete for the reason that the products of the hydrolysis, *viz.*, glycerin and fatty acid, are being constantly removed by diffusion. According to this view, therefore, no fat ever enters or leaves the epithelial cells as such, but as fatty acid and glycerin.

These two substances then enter the central lacteal, where equilibrium is again established and there is a large production of fat. This view derives support from the fact that fats and soaps exist side by side in the blood<sup>1</sup> in the serum of which Hanriot<sup>2</sup> has demonstrated the presence of a very powerful lipolytic enzyme. It is our intention to look for a lipolytic enzyme in the lymph and lymphatic tissue when the opportunity presents itself.

As is well known, lipase is by no means confined to the animal organism. It has been found by numerous observers in the resting and germinating seeds of various plants, but hitherto it has been looked upon as being concerned solely with the splitting of fats, especially during the period of germination.

On the other hand, Sachs<sup>3</sup> long ago pointed out that "the presence of fats in the seedling can only be explained by assuming that glycerin and the fatty acids travel from cell to cell, and are continually becoming re-united for the formation of fat," and quite recently Charabot<sup>4</sup> has also reached the conclusion that, in the plant, ethereal salts result from the direct action of the free acids on the alcohols. In view of these facts and of the results described in the above, it would seem logical to conclude that lipase can effect the formation as well as the decomposition of fats and ethereal salts in the plant, and that this ferment plays an important part not only in the utili-

<sup>1</sup> Hoppe-Seyler: *Ztschr. physiol. Chem.*, 8, 503.

<sup>2</sup> *Compt. rend.*, 123, 753 (1896).

<sup>3</sup> Sachs' "Plant Physiology," 1887, p. 347.

<sup>4</sup> *Bull. Soc. Chim.* [3], 23, No. 5.

zation and translocation of these important reserve materials, but also in the storing up of these substances in the seed and fruit.

### *Summary of Results.*

The results reached in this investigation may be briefly summarized as follows :

1. It has been found that ethyl butyrate is so easily hydrolyzed by lipase as to make it a very useful substance in the investigation of a number of problems connected with the chemical action of this enzyme.

2. By means of ethyl butyrate it has been possible to prove the presence of lipase in a number of organs and tissues in the animal organism, notably in the liver, stomach, and small intestine.

3. It has been shown that lipase is almost completely removed from its solutions by repeated filtration at ordinary pressure.

4. It has also been shown that lipase is a much more stable enzyme than has hitherto been supposed.

5. It has been shown that animal lipase hydrolyzes ethereal salts most rapidly at  $40^{\circ}\text{C.}$ , and that at  $65^{\circ}$  to  $70^{\circ}\text{C.}$  the enzyme is destroyed.

6. The conduct of lipase towards a few members of an homologous series of ethereal salts has been studied. It has been found that the stability of these ethereal salts towards lipase decreases with increase in molecular weight of the combined acid. The converse of this was found to be true for the hydrolysis of these ethereal salts by acids.

7. The effect of about twenty of the commoner antiseptics on lipase has been studied. By far the greater number of these substances have been found to exert a harmful effect on the enzyme. This was found to be particularly true of sodium fluoride and hydrofluoric acid and acids generally.

8. A study of the kinetics of the reaction has given the following results :

First, the velocity of the reaction is not proportional to the active mass of the ethereal salt. Secondly, the velocity of the reaction is nearly proportional to the concentration of the en-

zyme. Thirdly, the reaction is incomplete. This holds for all ordinary concentrations of the enzyme and the ethereal salt. With very concentrated or energetic extracts of the lipase or with very small amounts of ethereal salt the hydrolysis certainly approaches completion. Finally, the coefficient of velocity as calculated according to the equation for a reaction of the first order, is not constant, but shows a regular falling off as the reaction proceeds.

9. By means of lipase we have effected a synthesis of ethyl butyrate from butyric acid and alcohol, thereby proving that the hydrolysis of an ethereal salt as effected by this enzyme is a reversible reaction. Finally, the bearing of this result on fat absorption and the storing up and translocation of fatty reserve material in the plant has been briefly discussed in the above.

STATE COLLEGE OF KENTUCKY,  
LEXINGTON, Sept., 1900.

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## DERIVATIVES OF PHENYL ETHER.

BY A. N. COOK AND H. W. HILLYER.

Up to the present time diphenyl ether and its derivatives have been prepared by at least thirteen different methods and have been studied by no less than twenty-five different chemists. While the methods are numerous the yield in almost every case is remarkably small. The leading methods that have been used are as follows :

Diphenyl ether was prepared by Hofmeister<sup>1</sup> by the action of diazobenzene sulphate on phenol. The yield was small. By using the chloride instead of the sulphate and changing the conditions Hirsch<sup>2</sup> obtained a yield of 50 per cent of the aniline used.

Mertz and Weith<sup>3</sup> obtained a small yield of diphenyl ether by heating phenol with zinc chloride and also with aluminium chloride.

Gladstone and Tribe<sup>4</sup> made various methyl phenyl ethers by distilling the corresponding aluminium cresolates.

<sup>1</sup> Ber. d. chem. Ges., **3**, 747.

<sup>2</sup> *Ibid.*, **23**, 370.

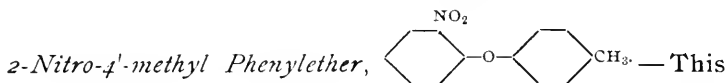
<sup>3</sup> *Ibid.*, **14**, 187.

<sup>4</sup> J. Chem. Soc. (London), **41**, 5; and **49**, 27.

Willgerodt<sup>1</sup> obtained a large yield of the trinitro derivative by heating picryl chloride and phenol in alcoholic solution with one molecular equivalent of potassium hydroxide.

One of the most productive methods which has been used is that originated by Haeusermann and Teichmann,<sup>2</sup> and also independently by F. Ullmann.<sup>3</sup> They heated potassium phenolate and several of its derivatives with various nitrohalogen derivatives of benzene and obtained, as a rule, good yields of nitro derivatives of phenyl ether. In approaching the study of phenyl ether derivatives this method was adopted and is here extended to reactions with the cresols.

For clearness in designation the nomenclature used by Haeussermann and Bauer<sup>4</sup> has been adopted.



compound was prepared by the action of *o*-bromnitrobenzene on potassium *p*-cresolate,<sup>5</sup> the reaction taking place according to the following equation :



One part by weight of potassium *p*-cresolate was heated in a small Florence flask, on a bath of fusible metal, with three parts of *o*-nitrobenzene to a temperature of 125° to 130°, when a vigorous action began, accompanied by a rise of temperature of several degrees. As soon as the action had ceased, which required about five minutes, the molten mass was cooled and extracted with ether. The ether extract was washed with a solution of potassium hydroxide to remove any free cresol which might be present. The excess of bromni-

<sup>1</sup> Ber. d. chem. Ges., 12, 1278.

<sup>2</sup> *Ibid.*, 20, 1446.

<sup>3</sup> *Ibid.*, 20, 1878.

<sup>4</sup> *Ibid.*, 20, 2083.

<sup>5</sup> The potassium cresolate was made by treating one part of paracresol with a molecular equivalent of potassium hydroxide dissolved in one part of water, evaporating to dryness on the water-bath with continual stirring and then drying in the air-bath at 100° C. for half an hour. This method yielded a very good product, which was of a slightly yellow color. An endeavor to prepare the cresolate by dissolving metallic potassium in the cresol, according to the method used by Haeussermann and Teichmann, and by Ullmann in working with phenol, yielded a dark, tarry product, which very materially effected the yield and purity of diphenyl ether made from it.



trobenzene was distilled off with steam, and the phenyl ether distilled under diminished pressure. Under a pressure of 25 mm. the substance boils at  $220^{\circ}\text{C}$ . The yield was one gram of the ether for every gram of the cresol used. On crystallizing it several times from alcohol it was completely purified, and on analysis yielded the following results :

	Calculated for $\text{NO}_2\text{C}_6\text{H}_4\text{OC}_6\text{H}_4\text{CH}_3$ .	I.	Found. II.
C	68.04	68.12	68.20
H	4.83	4.75	4.77
N	6.11	6.28	6.32

The compound melts at  $49^{\circ}$ . It distils with partial decomposition at ordinary pressure. It is not volatile with steam. It is very soluble in hot alcohol, but much less soluble in cold alcohol, from which it crystallizes in beautiful sulphur-yellow and apparently monoclinic crystals of considerable size. It is very soluble in ether, acetic acid, chloroform, benzene, and other organic solvents. It is sparingly soluble in petroleum ether. It is dissolved by concentrated sulphuric acid with slight charring and by concentrated nitric acid, which apparently oxidizes it.

*2-Nitrophenylether-4'-carbonic Acid*,  $\text{NO}_2\text{C}_6\text{H}_4\text{OC}_6\text{H}_4\text{COOH}$ .—This acid was prepared by dissolving the above-mentioned ether in glacial acetic acid, heating on the water-bath, and adding very slowly a cold solution of chromium trioxide in glacial acetic acid until a test portion failed to become turbid on diluting with a large amount of a dilute solution of sodium hydroxide. To accomplish this, three or four times the theoretical amount of chromium trioxide was necessary, a part of the acid formed being oxidized before all of the methyl compound was changed to acid. When the oxidation was judged to be complete, the acid was precipitated from the acetic acid solution by diluting with a large amount of water. It was purified by washing with water, dissolving in dilute ammonia, filtering, reprecipitating with hydrochloric acid, and recrystallizing two or three times from dilute alcohol. The yield in the first experiment was 24 per cent of the theoretical. Later experiments apparently yielded better results, but the resulting quantity of acid was not weighed. The pure nitro acid

melts at  $182^{\circ}$  to  $183^{\circ}$ . It is of a light yellow color and has no taste. It is slightly soluble in hot water, from which, on cooling, it crystallizes in radial tufts of needles. It is insoluble in petroleum ether and sparingly soluble in ordinary ether. It is very soluble in warm alcohol and glacial acetic acid. The acid was analyzed by determining the amount of silver in the silver salt, which yielded results as given below. In the second analysis the silver salt had darkened somewhat by being allowed to remain in contact with a solution of silver nitrate during the making.

	Calculated.	I.	Found.	II.
Ag	30.09	30.09		30.59

The alkali salts of this acid yield deep yellow solutions. The neutral solution of the ammonium salt yields precipitates with the following: Cupric sulphate, aluminic chloride, lead nitrate, manganous chloride, cobaltous chloride, magnesium sulphate, ferric chloride, ferrous sulphate, cadmium chloride.

The cadmium salt is white and crystalline. Nickel, calcium, strontium, and barium salts yielded no precipitates with the dilute solutions used. The silver salt, made by precipitating the neutral ammonium salt with silver nitrate, separates in light pink, curdy lumps. It is sufficiently soluble in water to yield a slight turbidity when hydrochloric acid is added. Its solubility was determined to be 1 part in 2180 parts of water at ordinary room temperature. When pure and dry it is very stable, and suffers no apparent change even when exposed to direct sunlight for several hours. It melts with decomposition at about  $220^{\circ}$ .

The barium salt is prepared by adding a slight excess of barium hydroxide to a strong solution of the ammonium salt, boiling off the ammonium, precipitating the excess of barium with carbon dioxide, and filtering hot. On cooling, the barium salt separates out in flesh-pink, pearly scales. One part of the salt dissolves in 122 parts of boiling water and in 948 parts of cold water. Before making an analysis it was dried over sulphuric acid for several days, and then heated in the air-bath for three or four hours at  $100^{\circ}$  to  $110^{\circ}$ . At about

100° it took on a much deeper hue, which seemed to be permanent.

	Calculated for $\text{Ba(R)}_2 + 1\frac{1}{2}\text{H}_2\text{O}$ .	I.	Found. II.
Ba	19.37	19.32	19.03
H <sub>2</sub> O	7.64	7.35	7.06

*2-Amido-4'-methyl Phenylether*,  $\text{NH}_2\text{C}_6\text{H}_4\text{OC}_6\text{H}_4\text{CH}_3$ .—The amido ether was prepared by dissolving the previously described nitro ether in alcohol and reducing with tin and hydrochloric acid while warming on the water-bath to 40° to 50°. During the reduction the solution was sky-blue, but when the reduction was complete it usually became pink. The end of the reaction was determined by taking out a test portion, and diluting with several times its own volume of water. When this failed to cause a turbidity due to the original substance the reduction was discontinued. The tin was precipitated with hydrogen sulphide, and, on concentration on the water-bath, the hydrochloride crystallized out in short, white needles, which are very stable when dry but unstable in contact with water. The salt melts at 220°. It is much less soluble in cold than in hot water. An attempt to prepare the free base was unsuccessful. It was precipitated from the hydrochloric solution, but decomposed in a bell-jar over sulphuric acid before it could be thoroughly dried.

The chloroplatinate was prepared by the usual method. It is of a greenish-yellow color, and melts with decomposition at 150°. The salt was dried over sulphuric acid for several days and then at 100° to 110° for three hours. The loss in weight corresponded to 1.5 molecules of water. On being heated it acquires a much darker tint, but on coming in contact with the air the surface immediately assumes its original color. It is very hygroscopic and gains weight rapidly while being weighed.

	Calculated.	Found.
Pt	24.1	24.1
H <sub>2</sub> O	3.23	3.03

Other work in similar lines is in contemplation to extend our present knowledge of the derivatives of phenyl ether.

## NOTE.

### *Notes on Industrial Chemistry.*<sup>1</sup>

It is difficult for the chemist who is not in direct touch with the industrial side of chemistry to keep informed of its rapid strides, and as the International Congresses held at Paris during the past summer presented a chance for the discussion of such matters the journals reporting the proceedings of these meetings contain much material that can with profit be brought to the attention of all who are interested in chemistry. In this paper a few of these matters will be briefly discussed.

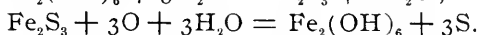
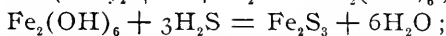
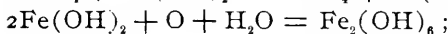
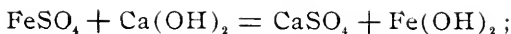
The electrolytic method for the preparation of the hydroxides of potassium and sodium can be carried out with greater success in the case of the former. While a number of factories prepare potassium hydroxide by the decomposition of a solution of potassium chloride, the chlorine being used to make bleaching-powder, only one factory in Germany decomposes sodium chloride by this method. The products are separated by means of a porous diaphragm or by the use of mercury, according to the Castner process as modified by Solvay.

The Solvay process, as used for the preparation of sodium carbonate, cannot be used for the preparation of the corresponding potassium compound. This is made by passing carbon dioxide through a mixture of magnesia and a saturated solution of potassium chloride, when a difficultly soluble magnesium potassium carbonate is precipitated. Part of the carbon dioxide is driven out by heat, and the potassium carbonate extracted by water.

Carbon dioxide and sulphur dioxide, which are prepared by burning coke and sulphur or sulphides, respectively, are purified by passing them into saturated solutions of their neutral salts and decomposing the acid salts thus formed with the evolution of the pure gases. The solutions of the neutral salts can be used repeatedly for this purpose.

The method of preparing potassium ferrocyanide by heating animal matter, potassium carbonate and iron, is still used in three German and some English and American works; but in Europe the main source of supply is coal gas. When a mixture of calcium hydroxide and iron sulphate is used to remove the hydrogen sulphide, the following reactions take place:

<sup>1</sup> Based on articles contained in the *Revue générale de Chimie*, Tome III, Nos. 1, 2, and 4; and in *Die chemische Industrie* for Oct. 1, 1900.



During this process the cyanogen compounds are also absorbed by the ferric hydroxide, and, after the mass has become useless on account of the accumulation of sulphur, they are isolated in the following manner: The mass, which contains sulphide of iron, sulphur, salts of lime, and free lime, ferrocyanides and sulphocyanides of iron and ammonia, is treated with water to remove the soluble part, and the residue, after treatment with lime to form the calcium ferrocyanide, is converted, by the action of potassium chloride, into an insoluble compound of potassium and calcium ferrocyanide, which is decomposed by potassium carbonate with the formation of potassium ferrocyanide. In one English factory the gas is passed through a solution of an iron salt and the Prussian blue formed is decomposed by caustic potash. In one factory in Germany the "vinasses" are heated and the cyanogen compounds formed from the decomposition of the trimethylamine are converted into Prussian blue as in the other method. In 1899 the production of potassium ferrocyanide in France, Germany, England, Belgium, Holland, and the United States amounted to 10,500 tons, of which 50 per cent was converted into potassium cyanide. Potassium sulphocyanide, which is also obtained from the coal gas, is only made in comparatively small quantity and is converted into a copper salt which is used as a constituent of paint for the hulls of vessels. This copper salt acts as a poison to the crustacea which foul the hulls of ships.

Potassium cyanide, which, since its introduction as a solvent for gold in extracting the latter from its ores, has been manufactured in such quantities, is prepared almost entirely by one method, that of Rössler and Hasslacher. After the introduction of the electrolytic method for the preparation of aluminium some disposition had to be made of the metallic sodium which had formerly been used in the preparation of this substance. This problem was solved by the introduction of a method for the preparation of potassium cyanide which was very simple and in which the sodium could be used. By its action on potassium ferrocyanide a mixture of potassium and sodium cyanides and iron is formed. By washing and crystallizing the product, the substance which is sold under the name of potassium cyanide is obtained in such amounts and so cheaply that it has displaced the synthetical method

and the Liebig method, in which the ferrocyanide was treated with potassium carbonate. Attempts have been made to utilize the nitrogen of ammonia for the preparation of potassium cyanide; but the processes devised for this purpose are as yet in the experimental stage. About 7500 tons of the cyanides, which are used in the extraction of gold and in plating on account of the formation of soluble double cyanides, were manufactured in 1899.

The amount of sulphuric acid manufactured has been steadily increasing from year to year at a rapid rate. The following figures of the industry in Germany will perhaps give a clearer idea of the change: In 1882 the amount was 358,149 tons; in 1890 the amount was 627,392 tons; and in 1897 the amount was 845,582 tons.

As yet very few of the mechanical ovens for roasting the ores have been introduced into Germany, although they are used in a number of factories in the United States. The ovens used in Europe are of the Perret-Malétra type, with 4, 5, or 6 plates, in which the source of heat is the burning sulphur, if fine ore is to be used; but in some places a series of muffles are placed one above another and the zinc blend is roasted by the passage of the hot gases over the muffles in succession, while the ore is removed from a higher to a lower muffle as the process proceeds.

There has been practically no change in the Glover tower except the introduction, in several cases, of two small towers in place of one large one.

Each manufacturer or builder has his own peculiar idea regarding the size and shape of the leaden chambers, some using several large ones, and others a number of small ones. The usual size of the chambers in Europe is  $8 \times 12$  meters, while in America the manufacturers often use 12 chambers 8 meters long. The general shape is that of a parallelopiped; but many devices have been introduced to bring about a more thorough contact of the gases and so produce a better yield. In some cases the entrance tubes for the gases are arranged tangent to the sides and the exit tubes at the centre, so that a circular motion is imparted to the gases. In others, one chamber is placed inside of another, thus economizing space and overcoming, to some extent, the fluctuations in temperature. In some furnaces devices are used to cool the interior of the chamber, such, for instance, as columns or pipes, through which cool air can circulate, extending up into the chambers. The Glover tower has greatly increased the efficiency of the process, as 15 to 20 per cent of the acid is formed

there. The amount of nitrate used to produce 100 kilograms of the monohydrate varies from 0.83 to 1.12 kilograms.

In the concentration of the acid in platinum vessels great care has to be observed to prevent a loss of platinum, as a small amount of impurity may produce a marked effect. The purer the acid the less the danger of attack; but with acids of equal purity the amount of loss increases with the concentration. For many years acid of 93 per cent monohydrate was considered satisfactory for all purposes; but the demand for an acid of 95 to 98 per cent has necessitated the introduction of other material than platinum for concentration vessels, and one of platinum and gold is now used with success for this purpose. A vessel which can furnish 10,000 to 12,000 kilograms in twenty-four hours would have to contain 56 kilograms of pure platinum; but one containing 52 kilograms of platinum and 4 kilograms of gold can be used to greater advantage as the loss in the case of the platinum vessel is 1 gram per ton and, at the highest, 0.1 gram per ton for the platinum and gold vessel, a saving of about \$940 a year. The latter also requires less heat and less attention. An alloy of platinum and cast-iron and simple cast-iron vessels have been used with some success if the material is carefully selected. Of course the deterioration is more rapid, but the loss is proportionately no greater and the amount invested is much less. Porcelain vessels have also been used for this purpose.

Within a few years a method for the preparation of sulphuric acid has been introduced which does not necessitate the use of the cumbersome leaden chamber, but is based on an observation made by Berzelius of the influence of one substance in producing a reaction between two other substances without itself undergoing any change. He called this catalytic action, and substances of this nature were called contact substances. A number of observers have repeated the experiments made in 1831 by Philipps, when sulphurous acid and oxygen were made to combine by the presence of a third substance, and have attempted to apply this method for the preparation of sulphuric acid on the large scale. Winkler and others have used platinum asbestos as the contact substance; but all efforts in this direction for several years led to the conclusion that the method was only applicable to the preparation of the fuming sulphuric acid with a maximum yield of 67 per cent.

In 1898 an observation was made which rendered it possible to use this method with great success, and at the present time at least eight firms are preparing the acid by this method. It was found necessary to reduce the temperature of

the gases in order that they might combine, and this can be done in a number of ways. This method has probably not been generally adopted on account of the lack of knowledge of the details, and a belief that it is as yet only in the experimental stage. The royalty is also high and owners of the old style plants cannot afford to cast these aside at once, and in fact there is still doubt as to the part this improvement will play in the industry.

As yet the price has not been affected; but when the supply from this source increases, the chamber acid methods may have to be improved to enable them to compete with the new method, and the matter may adjust itself by a division of labor, when the concentrated acid will be made by the contact method and the dilute acid by the chamber process at a profit to the manufacturers of each.

The advantages claimed for the new method are a large economy in space, a reduction in capital invested of 30 to 40 per cent, and the saving of all expense for nitrate or concentration. The price of this acid is, however, 15 per cent less.

J. ELLIOTT GILPIN.

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## REVIEWS.

LEÇONS DE CHIMIE PHYSIQUE, PROFESSÉES A L'UNIVERSITÉ DE BERLIN. PAR J. H. VAN'T HOFF, Membre de L'Académie des Sciences de Berlin, Professeur Ordinaire a L'Université et Directeur de L'Institut de Physique de Charlottenbourg. Ouvrage traduit de L'Allemand par M. CORVISY, Professeur agrégé au Lycée de Saint-Omer. Troisième Partie. Relations entre les Propriétés et la Composition. Avec un Portrait gravé de l'auteur. Librairie Scientifique, A. HERMANN. Paris, 1900. pp. 153.

The appearance in French of the first and second parts of Van't Hoff's "Vorlesungen" has already been noted in this Journal (Vol. 23, 531). It only remains to call attention to the completion of the French edition. The strong desire on the part of chemists in France to keep in touch with the latest developments in physical chemistry, is shown by the short time which has elapsed between the appearance of the German original and the French translation of this brilliant work. The earlier parts appeared in French some time before the German edition was completed, and the third and last part has been published in French in less than a year after it appeared in the original.

As will be seen from the title-page this part of the book deals with relations between properties and composition. Two classes of properties are taken up—physical and chemical—and the effect of composition upon each pointed out.



The book as a whole, including dynamics, statics, and relations between properties and composition, can scarcely be regarded as a systematic and comprehensive text-book on physical chemistry, nor does it pretend to be such. We find, however, in this work all of the most important phases of physical chemistry discussed, and like all work from the pen of Van't Hoff, it contains new and suggestive ideas at every turn. This book is not adapted to the beginner in physical chemistry, but is essential to every one who would teach this branch of science.

H. C. J.

EINFÜHRUNG IN DIE STÖCHIOMETRIE, ODER DIE LEHRE VON DER QUANTITATIVEN ZUSAMMENSETZUNG DER KÖRPER UND IHREN MIT DIESER ZUSAMMENHÄNGENDEN EIGENSCHAFTEN, MIT RECHENBEISPIELEN. Für Studierende und Chemiker. Von DR. JOACHIM BIEHRINGER, a. o. Professor an der Herzoglichen Technischen Hochschule zu Braunschweig. Mit 18 Abbildungen und einer Tafel. Friedrich Vieweg und Sohn. Braunschweig, 1900. pp. 498.

Many of the works on stoichiometry which have hitherto appeared have been rather dry reading. This is partly due to the nature of the subject. Most of the relations which have been established in this field are purely empirical, and we have little or no conception as to what they mean. It is not a simple matter to present such relations in an attractive and interesting form. The book in hand, however, is interesting reading. The author has shown how it is possible to deal in an attractive manner, with facts which are not correlated by any wide-reaching generalization. This has been accomplished, in the first place, by a complete mastery of the material in hand, and, in the second place, by an unusually clear and lucid method of presentation.

This book covers rather more ground than the average work which deals with the subject of stoichiometry even in a broad way. This will be seen from the contents. Division one, on the laws of combination and the atomic theory, includes the laws of definite and multiple proportions and the historical development of the atomic theory. The second and third parts of the book deal with gases and liquids, and especially the physical properties of matter in these states of aggregation.

Division four is devoted to solutions, and here some of the fundamental conceptions of the newer physical chemistry are introduced. A large part of this division of the book is given up to the theory of dilute solutions, including a discussion of osmotic pressure, lowering of freezing-point, rise in boiling-point, methods of determining molecular weights in solution, etc.

The physical properties of solids are taken up after solu-

tions, and division six is devoted to relations between the atomic weights, including, of course, the Periodic System.

There might be some question as to the best order of arrangement of the material in the latter part of the book. As we have now so many well-defined examples of solid solutions, would it not be better to study gases, liquids, and solids, and then take up solutions in a broad way, including mixtures of matter in every state of aggregation with matter in the same and every other state?

Again, ought not any relations between the atomic weights be pointed out directly after the methods for determining atomic weights have been considered?

These questions are not raised with any desire to criticize the book. It is obvious that these are minor points and in no wise detract from its great merit. It is not too much to say that Biehringer has given us one of the most readable and valuable books on stoichiometry which has ever been published.

H. C. J.

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